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AN EXPERIMENTAL STUDY ON THE EFFECT OF A JET FUEL/FREE WATER MIXING PROCESS ON JET FUEL PHYSICOCHEMICAL PROPERTIES

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ABSTRACT

The aviation fuel of grade Jet A1 is one of the most used petroleum-derived jet fuels worldwide. The aviation industry, in coordination with standards setting organizations, has developed specifications, fuel handling practices and quality control procedures to ensure the integrity of jet fuel throughout its supply chain. A key aspect of jet fuel integrity is its potential contact and mixing with traces of free water, which occurs regularly in aviation fuel systems. The aim of this work was to perform an experimental evaluation of the effect of a mixing process of free water and jet fuel on chemical composition and fuel properties. The most relevant change in chemical composition occurred in the total content of naphthenic hydrocarbons. Specifically, a decrease in the content of naphthenic hydrocarbons with a lower number of carbon atoms per molecule was identified. Since the water content of all tested samples was similar, the changes in composition and physical properties were due to a loss of volatile compounds induced by the mixing process. Accordingly, there was an increase in density (decrease in API gravity), flash point, kinematic viscosity, initial boiling point, and the T10 point.

Keywords: aviation fuel, jet A1, water mixing, hydrocarbon families, physical properties.

INTRODUCTION

Petroleum-derived jet fuels are mixtures of hydrocarbons and do not have a fixed chemical composition; they are produced to meet a group of key fuel performance properties. International standard organizations, government agencies and the aviation industry have developed specifications, fuel handling practices, and quality control procedures to ensure the jet fuel integrity along its entire supply chain. A key aspect of jet fuel integrity is water contamination, which has been identified as a potential cause of aircraft incidents and accidents (Pour MJ and G, 2017). The presence of trace water can cause several problems: promotion of corrosion in fuel system components, reduction of fuel energy content, promotion of microbiological growth, variations in cold flow properties, and formation of ice crystals (Baena-Zambrana *et al.*, 2013; West *et al.,* 2018). Water can be present in jet fuels in three forms: dissolved, suspended as water-in-fuel emulsions, or free water (Baena-Zambrana *et al.*, 2013; Hemighaus *et al.,* 2006; West *et al.*, 2018; Wu *et al*., 2017). Free water forms a separate layer at the bottom of storage tanks. Naturally occurring surfactants and surfactants formed during the refining process, such as naphthenic acids and sulfonic acids, are known to stabilize water emulsions in jet fuels (Johnson, 2018). Dissolved water in fuel is in parts per million and depends on various factors such as fuel composition, temperature, gas pressure in the upper part of the liquid layer and atmospheric humidity (Wu *et al.*, 2017). Water solubility rises with increasing temperature, atmospheric pressure, and humidity. Dissolved water can be a significant problem since there is no physical way to remove it from the fuel. It is simply pumped into the aircraft. If fuel temperature reduces to below zero degrees, dissolved water could come out of solution as free water. If enough water is present, it can form ice crystals, with risk of blocking small orifices and fuel lines and filters. It has been widely reported that water solubility increases with fuel aromatic content (Baena-Zambrana *et al.,* 2013). Single ringed aromatic compounds dissolve 5-10 times more water than similar saturated compounds (Johnson, 2018). Research related to the effect of chemical composition on water solubility becomes more relevant as more hygroscopic jet fuels could be used.

Most research related with jet fuel-water interaction has been focused on predicting water solubility at different ambient conditions and fuel compositions (Wu *et al.,* 2017), understanding the physics behind the behavior of water in different hydrocarbons and jet fuels at low temperatures (Baena-Zambrana *et al*., 2013; Murray *et al.,* 2011), and developing additives such as icing inhibitors (West *et al.*, 2018). To the best of our knowledge, there are not reported investigations related to the effect of water-jet fuel interaction on key fuel properties. As reported by Baena-Zambrana *et al.* (2013), there are several means by which jet fuels can be contacted by free water, including: rain water entering through seals and hatches of fuel storage tanks, water left behind after cleaning operations in tanks and transport vehicles, condensation of water from moist air, and precipitation of dissolved water (Baena-Zambrana *et al.*, 2013). If both liquids in contact undergo mixing and agitation processes, even at low water concentrations (order of ppm), changes in chemical composition and therefore changes in fuel properties can occur. The aim of this work is to carry out an experimental evaluation of the effect of a mixing process of free water and jet fuel on chemical composition and key fuel properties.

MATERIALS AND METHODS

Preparation of Jet Fuel/Water Mixtures

The jet fuel herein studied complied with the Jet A1 fuel specifications established in the ASTM D1655 standard (ASTM, 2020) and was supplied by a Colombian wholesale distributor. The fuel was freshly sourced, and its homogeneity and stability were guaranteed by storing it in a glass container and in an environment with a controlled temperature between 20 °C to 23 °C. Before the mixing process with water, the jet fuel was filtered to remove impurities and suspended solids. To prepare each mixture (9 mixtures in total), 500 ml of jet fuel were transferred to a 1000 ml glass container and then a measured amount of distilled water was added. Then, each mixture was gently stirred with a magnetic stirrer for at least 16 h until no drop of water was observed. According to Lam et al., this time is sufficient for a jet fuel/water system to reach equilibrium (Lam *et al.,* 2014). During the mixing process the temperature was controlled between 20 °C to 23 °C. In all cases, the amount of added water in ppm in relation to the mass of fuel was above the value of water solubility commonly reported for jet fuels.

Physicochemical Characterization of Jet Fuel/Water Mixtures

The procedure for composition quantification implemented in this study was based on the method described in the ASTM D2425 Standard Test Method for Hydrocarbon Types in Middle Distillates by Mass Spectrometry (ASTM, 2017) and the method developed by Gehron and Yost, Hydrocarbon-Type Analysis of Jet Fuel with Gas Chromatography/Mass Spectrometry (Gehron *et al.,* 1989). Samples were analyzed using an Agilent Technologies 7890A gas chromatograph linked to a 5975C mass selective detector. A non-polar DB-5HT GC column manufactured from (5%-Phenyl)-methylpolysiloxane was used. Oven temperature was set at 45 °C for 10 min and then increased to 300 °C at the heating rate of 5 °C/min. Samples were prepared using a standard solution of methyl palmitate (0,37 mg/ml) in carbon disulfide. The integration parameters were properly modified to get between 140 and 160 signals in the chromatogram and facilitate the identification of compounds in agreement with the data base available (NIST 2017). The quantification method allowed determining the content in mass percent of five hydrocarbon families: paraffinic, naphthenic, aromatic or benzenic compounds, naphthalene, tetralin and indane derived compounds. The analytical standards Supelco n-Paraffin Mix 47100 and n-Paraffin mix 47102 were used for the analysis of the first family. In the case of the second and third families, the analytical standards Restek DHA Naphthene 30728 and DHA Aromatic Standard 30729 were used, respectively. Naphthalene of analytical grade was used for analyzing the fourth and fifth families.

Physical properties of the jet fuel/water mixtures were measured using the corresponding ASTM standard test methods as shown in Table-1. The quality of conformance of the tested samples was evaluated according to the specifications established in the ASTM D1655 standard (ASTM, 2020). The water content of all samples was determined by the coulometric Karl Fischer titration method according to the ISO 12937 - 2001 (UNE, 2001) standard.

Table-1. Physical properties measured for the tested samples.

Fuel property	Standard test method
Heat of combustion ((kJ/kg)	ASTM D 240 (ASTM, 2019a)
Distillation properties (°C)	ASTM D 86 (ASTM, 2019b)
API gravity (° API)	ASTM D 287 (ASTM, 2019c)
Freezing point (°C)	ASTM D 2386 (ASTM, 2019d)
Kinematic viscosity at -20 °C (cSt=mm^2/s)	ASTM D 445 (ASTM, 2019e)
Flash point (°C)	ASTM D 56 (ASTM, 2016)

Experimental Plan

Table-2 shows the experimental plan carried out to evaluate the effect of water mixing in jet fuel properties. The concentration levels of the water added to the mixture were selected according to a series of pre-tests. The level 0 corresponds to a jet fuel stored in a desiccator (neat fuel) and the level 1 to a jet fuel exposed to air humidity. Levels 3 to 11 correspond to different amounts of added water from 100 ppm to 10000 ppm in relation to the weight of the jet fuel used. The response variables are fuel composition (five hydrocarbon families) and the fuel properties listed in Table-1. To understand the relationships between variables and their relevance to the problem being studied, univariate and multivariate statistical analyses were carried out using the free software R version 3.6.2. For each level of added water two set of tests were carried out (24 samples in total).

RESULTS AND DISCUSSIONS

Statistical Analysis

The pattern of response to the different variables considered in the experimental plan was described by means of a univariate analysis. As can be seen in Table 3, most variables have a coefficient of variation less than 10% which indicates low levels of dispersion around the mean. However, the data of naphthenic and naphthalene contents show greater but moderate variability, while in the case of the indane and tetralin compounds their content undergoes high changes. As shown in Table-3, the content of the indane and tetralin compounds was the lowest in comparison with the other hydrocarbon families (0,1% in average).

With the aim of performing a graphical representation of the multivariate data obtained, a Biplot analysis was carried out (see Figure-1). This exploratory graph represents the data of the levels of added water

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(samples) but also the response variables, enabling to interpret relationships, trends, approximate correlations, and variances existing in the data.

By numbering the quadrants from 1 to 4 in the Biplot graph, starting from the upper right corner and turning clockwise, some relationships between the levels of added water and response variables can be analyzed.

Table-2. Experimental plan. Jet fuel/water mixing process.

Level	Input variable	Response variable	
	Amount of added water (ppm)	Composition (family of compounds)	Fuel properties
0	Neat fuel	Paraffinic Naphthenic Aromatic Naphthalene Tetralin and indane	Heat of combustion Distillation (4 points) API Gravity Freezing point Flash point Kinematic viscosity
1	Sample exposed to air humidity (10 ppm)		
2	100		
3	200		
4	300		
5	500		
6	700		
7	1000		
8	1500		
9	3000		
10	5000		
11	10000		

Table-3. Univariate statistical analysis of the data obtained (14 response variables and 24 samples).

Measured variable	Average	Standard Deviation	Coefficient of Variation	Minimum	Maximum
API Gravity at 60°F (15,56 °C)	**40,85**	**0,8**	**1,95%**	**38,7**	**41,7**
Flash Point (°C)	55,6	8,58	15,44%	43	78
Freezing Point (°C)	-51,92	2,31	-4,44%	-54	-45
Viscosity at -20°C (cSt)	6,2	1,01	16,32%	5,49	9,16
Gross combustion heat (kJ/kg)	45984,1	37,08	0,08%	45915	46062
Initial Boiling Point (°C)	168,33	13,87	8,24%	149,5	207
T10 (°C)	188,81	10,54	5,58%	176,5	216,5
T50 (°C)	215,58	4,96	2,3%	209	228,5
Final Boiling Point (°C)	280,54	1,7	0,61%	278	284,5
Total Paraffinic	89,28	2,04	2,28%	85,63	92,84
Total Naphthenic	3,38	1,32	39,07%	1,42	5,9
Total Aromatic	4,38	0,92	21,06%	2,96	6,68
Total Naphthalene	2,87	0,98	34,18%	2	5,21
Total Tetralin and Indane	0,1	0,08	85,45%	0	0,24

Regarding to the levels of added water, the following trends can be observed in the biplot graph: 1) Because they are close and scattered in all quadrants, the samples with quantities of added water from 100 ppm to 1500 ppm have similar behavior; 2) Being located at the end of the second quadrant, the samples corresponding to levels of added water of 5000 ppm and 10000 ppm have the most atypical behavior; 3) Similarly, but to a lesser extent, the samples corresponding to the neat fuel and the fuel exposed to air humidity, localized in the first quadrant also have a differentiated behavior. On the other hand, when the relationships among response variables are

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analyzed, the following trends can be inferred: 1) Since they are apart from other variables, the heat of combustion, total paraffinic content and total aromatic content do not present strong correlations with any variable; 2) The API gravity, located on the X-axis and the total naphthenic content, located in the first quadrant, have a strong correlation with the rest of the variables (they are inverse relationships due to the negative coefficients); 3) The other response variables overlap on the graph and are therefore strongly correlated. Additionally, the statistical tool allows to analyze multiple relationships among

samples and variables as follows: 1) Samples with an added amount of water of 3000 ppm have the strongest effect on most response variables, with the exception of heat of combustion, API gravity, and total content of paraffinic, and aromatic compounds; 2) Samples corresponding to neat fuel (0 ppm of water), fuel in contact with air humidity and 100 ppm of added water have the strongest effect on the total naphthenic content; and 3) Samples with an added amount of water of 200 ppm and 500 ppm have the strongest effect on API gravity.
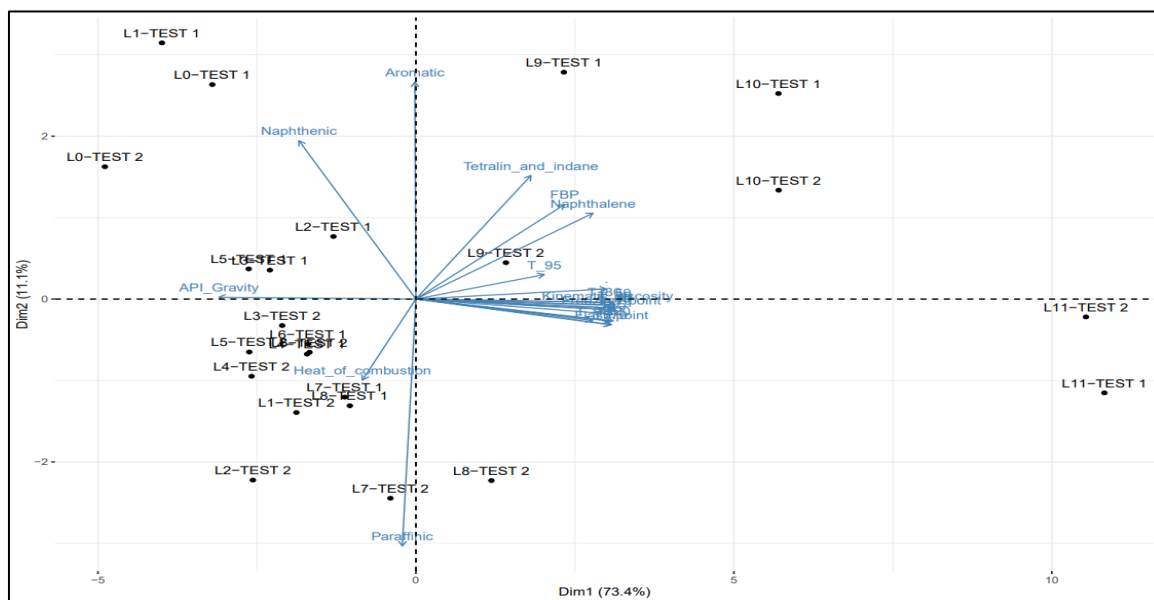

Figure-1. Biplot graph of the experimental data (levels of amount of added water and response variables).

For those response variables that showed the strongest statistical dependence with the amount of added water (W in ppm), generalized linear models were obtained as shown in Table-4. The values of the

determination coefficients (R-squared) indicate that at least 85% of the variability of the response variables is explained by the levels of added water considered.

Table-4. Generalized linear models for response variables.

Model equation	R^2 (%)
$API\ Gravity = 41{,}35 - 0{,}00026 * W$	99%
$Flash\ Point\ (°C) = 50{,}37 + 0{,}002814 * W$	99%
$Freezing\ Point\ (°C) = -53 + e^{1{,}632 + 0{,}0007807 * W}$	96%
$Kinematic\ Viscosity\ (at - 20°C)\ (cSt) = 5{,}57 + 0{,}0003416 * W$	98%
$Initial\ Boiling\ Point\ (°C) = 168{,}33 + 0{,}004634 * W$	99%
$T10\ (°C) = 188{,}2 + 0{,}003541 * W$	97%
$T50\ (°C) = 212{,}5 + 0{,}001642 * W$	96%
$Total\ Naphtenics\ (\%) = 3{,}785 + 0{,}0002197 * W$	85%

Effect of the Jet Fuel/Water Mixing Process on Chemical Composition

Figure-2 shows the composition of the tested samples by hydrocarbon families. As expected for jet

fuels, the paraffinic family accounts for the highest mass percentage of the fuel (89,3% in average). As can be seen in Figure-2(a), the paraffinic content tends to remain constant as the amount of added water increases. The low

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value of the standard deviation indicates that all values tend to be close to the mean (see Table-3). Similar trends are observed for the aromatic (Figure-2(c)) and indane and tetralin contents. The tetralin and indanes compounds have the lowest percentage (0,1% in average). In the case of the naphthenic content (3, 38% in average), Figure-2(b) shows that it decreases as the amount of added water increases for both tests. In the case of the second test, the naphthenic weight percent changes from a maximum value of 5,9% for the neat jet fuel to a minimum value of 1,42% for the mixture with 1500 ppm of water. Regarding to the naphthalene content, it remains stable from the level 0 (neat fuel) to the level 8 (1500 ppm of water), and then, in the case of the second test, it increases with the amount of added water, from 2, 13% (1500 ppm of water) to 5, 21% (10000 ppm of water).

The procedure for compositional analysis implemented in this study also allowed quantifying individual hydrocarbon components. A total of 122 components were identified, 56 paraffinic, 31 aromatic, 21 naphthenic, 11 naphthalene and 3 tetralin and indane compounds. In the case of naphthenic hydrocarbons, there is a noticeable reduction in the content of various of them, when the neat fuel and the mixtures with an amount of added water above 3000 ppm are compared. The greatest changes occurred in the content of the components called, Naphthenic 2 (Methylcyclohexane, C_7H_{14}), Naphthenic 3 (1,4-dimethylcyclohexane, C_8H_{16}), Naphthenic 5 (1, 1, 4-trimethylcyclohexane, C_9H_{18}) and Naphthenic 10 (Propyl cyclohexane, C_9H_{18}). These cyclic, saturated, and branched hydrocarbons are among the lightest components of the jet fuel tested. By comparing the same samples, an increase in the content of 5 naphthalene compounds was also determined.
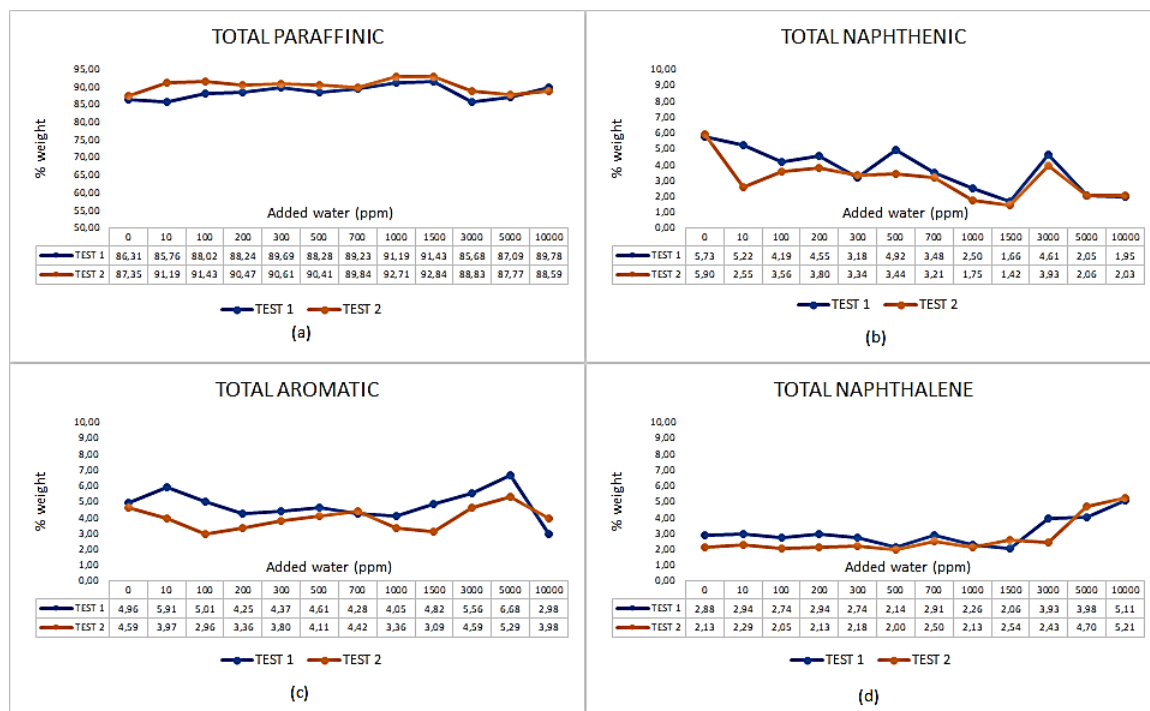

Figure-2. Composition of the tested samples expressed as total content of hydrocarbon families.

Effect of the Jet Fuel/Water Mixing Process on the Jet Fuel Water Content

To evaluate the effect of the mixing process on water solubility, the water content of each sample considered in the experimental plan was measured once the mixing process was completed. For the two samples corresponding to the neat fuel, an average water content of 53, 3 ppm was obtained. Considering all samples (24), an average value of 53,6 ppm was obtained with a standard deviation of 3.16 ppm.

Water solubility results indicate that the changes reported in the chemical composition of the tested samples are not due to an increase in the water content of the fuels. Most likely, these changes are due to loss of volatile components induced by the mixing process. In fact, the individual naphthenic compounds, mentioned before, tend to be concentrated in the lower boiling fractions of a typical jet fuel.

Effect of the Jet Fuel/Water Mixing Process on Jet Fuel Properties

The effect of the jet fuel/water mixing process on selected jet fuel properties is shown in Figures 3 to 8. These figures also show the conformity assessment of the fuel samples which allows to verify their compliance (conformance), noncompliance (non-conformance) or uncertainty (nothing can be said) with respect to the ASTM D1655 Standard (ASTM, 2020).

As can be seen in Figure-3, the gross heat of combustion of all samples (both tests) shows a low

variation (45984,1 kJ/kg in average). It indicates that this property was not significatively affected by the fuel jet/water mixing process in the range of added water studied (from 100 ppm to 10000 ppm). The conformity assessment indicates that all samples comply with the quality control limit (QCL) fixed for this property.
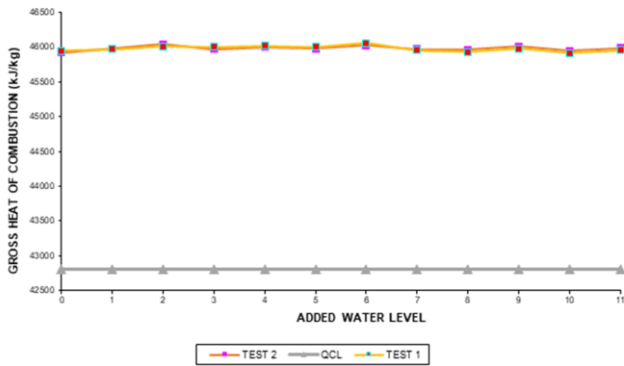

Figure-3. Effect of the jet fuel/water mixing process on the gross heat of combustion.

Figure-4 shows the effect of the mixing process on the distillation properties of the tested samples. Four points of the distillation curve were considered, the initial boiling point (IBP), the temperature of 10% of distilled volume (T10), the temperature of 50% of distilled volume (T50) and the final boiling point (FBP). For both replicates, a gradual increase in the IBP is observed as the quantity of added water increases from level 0 (neat jet fuel) to level 8 (1500 ppm). From level 8 to level 11 (10000 ppm), the increase in IBP becomes more noticeable. For the last sample, the value of IBP is slightly greater than the maximum allowed value for the T10 point or QCL value (205°C) and so it can be considered as a non-conforming sample. This result indicates that the mixing process caused losses of the lighter hydrocarbon components. A similar trend is observed for the T10 point which enters in the uncertainty zone in the case of the sample corresponding to level 10 (5000 ppm) and is outside of specification (non-conforming) for the sample corresponding to level 11 (10000 ppm). Regarding to the middle and end points of the distillation curve (T50 and FBP), it can be inferred from Figure 4 that they do not show any significative change within the range of added water analyzed.
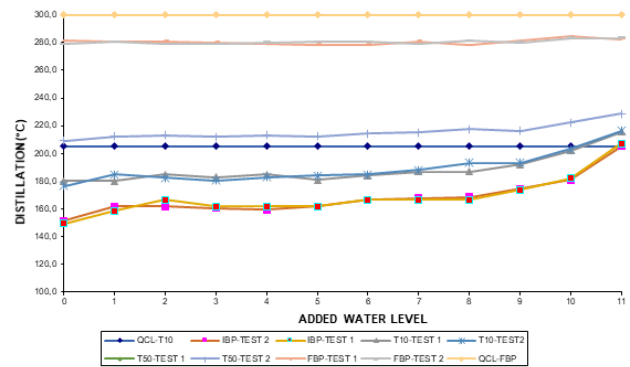

Figure-4. Effect of the jet fuel/water mixing process on distillation properties.

As shown in Figures 5 to 8, the API gravity, flash point, freezing point, and viscosity undergo more significative changes from values of the quantity of added water above 1500 ppm, as occurs in the case of the IBP and the T10 point. The changes observed, decreasing API gravity (increasing density) and increasing IBP, T10, flash point, viscosity, and freezing point, indicate losses of the lighter components due to the jet fuel/water mixing process. Despite the mentioned changes, all samples comply with the specifications for API gravity (Low Quality Control Limit, LQCL, and Upper Quality Control Limit, UQCL) and flash point established by the ASTM D1655 Standard (ASTM, 2020). In the case of the properties related with the fluidity of the jet fuel (viscosity and freezing point), it is observed that the sample with the highest added water is out of specifications for both properties.
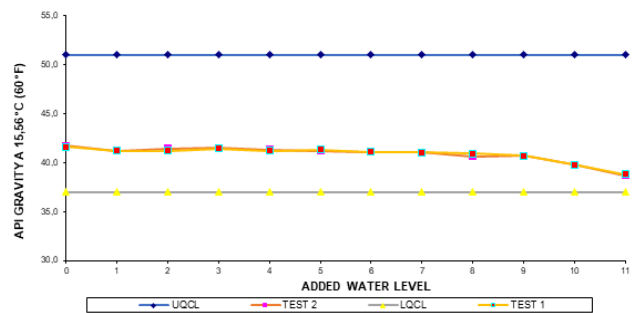

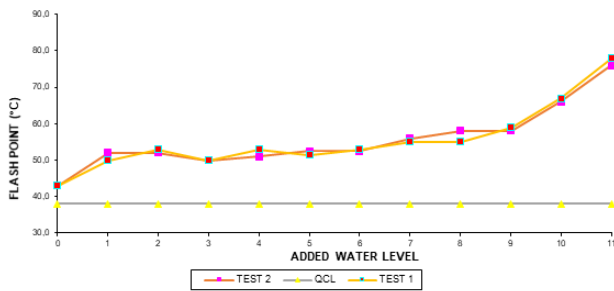**Figure-5.** Effect of the jet fuel/water mixing process on API gravity.

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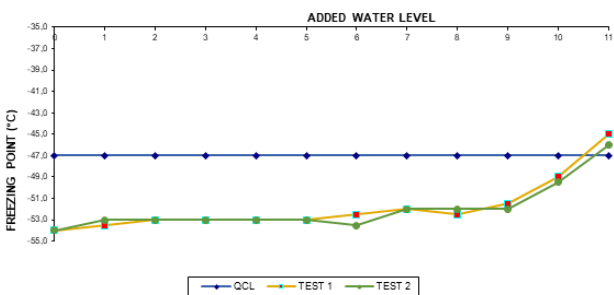**Figure-6.** Effect of the jet fuel/water mixing process on the flash point.

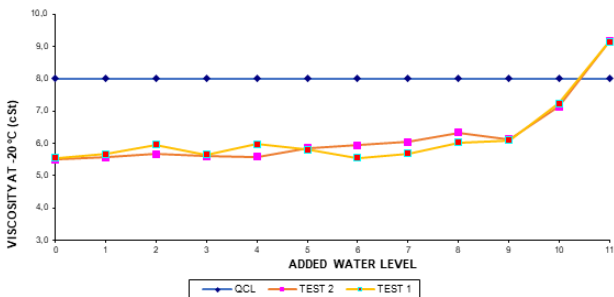**Figure-7.** Effect of the jet fuel/water mixing process on the freezing point.

Figure-8. Effect of the jet fuel/water mixing process on kinematic viscosity at -20°C.

CONCLUSIONS

The jet fuel/water mixing process carried out in this experimental work resulted in some changes in the chemical composition and physical properties of the tested jet fuel. Such changes were more noticeable for values of the amount of water added higher than 1500 ppm.

The most relevant change in chemical composition occurred in the total content of naphthenic hydrocarbons. As the amount of water added increased, the naphthenic content decreased. Specifically, a decrease in the content of naphthenic hydrocarbons with a lower number of carbon atoms per molecule was identified. This type of hydrocarbons is found in the jet fuel fractions with a lower boiling range.

Since the water content of all tested samples was similar, the changes in composition and physical properties were due to a loss of volatile compounds induced by the mixing process. Accordingly, there was an increase in density (decrease in API gravity), flash point, kinematic viscosity, initial boiling point, and the T10 point.

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