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Influence of Adding High Flash Point, Special Jet Fuel for Brazilian Navy (QAV-5), in Brazilian Marine Gasoil (ODM), on Fuel Viscosity, Specific Gravity, Cetane Index and Lubricity

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The degradation of Type 5 aviation kerosene, used in navy aircraft, (QAV-5) during the storage period was evaluated by thermal oxidation test (JFTOT) and current gum test. QAV-5 failed to meet jet fuel specifications after 16 weeks of accelerated aging, due to compromised thermal stability and substantial gum generation. Pure blends of QAV-5 and aviation kerosene and marine diesel oil (QAV-5/ODM) in proportions of 25, 50 and 75% (v/v) were analyzed according to the marine diesel oil (ODM) specification, in week zero and at intervals of four weeks throughout the aging process. Fuel viscosity, specific gravity, cetane number and lubricity decreased as the QAV-5 content in the mixture increased. The viscosity of QAV-5, however, increased with storage time. The employment of pure QAV-5 diesel engines is not advisable unless the use of aviation fuel is expressly permitted. By the fuel haze lubricity test (FLHT), QAV-5/ODM blends with up to 88% (v/v) QAV-5 content can be used in diesel engines without damaging the fuel system. However, confirmation by standard high frequency reciprocating rig (HFRR) testing would be advisable for QAV-5/ODM mixtures with QAV-5 volumetric content above 75%.

Keywords: QAV-5, ODM, jet fuel, marine gasoil, storage stability, accelerated aging

Introduction

The main fuel used by the Brazilian Navy for aircraft propulsion is the high flash point, special jet fuel for Brazilian Navy (QAV-5), whose specification is similar to that of international military jet fuel JP-5.[1,2] QAV-5 is a Brazilian Navy exclusive product and its specification requires a minimum flash point of 60 °C, meanwhile commercial jet fuels (Jet A and Jet A-1) require a minimum flash point of 38 °C.[1,3] For safety reasons in confined environments, it is internationally agreed that the flash point of fuels stored aboard ships must be at least 60 °C, as a rule.[4] Therefore, QAV-5 high flash point enables it to be stored on Brazilian Navy ships, supplying aircraft on missions and other operational activities at sea.

However, if QAV-5 remains stored on ships for a long period, the fuel oxidation process can alter some of its characteristics, especially if jet fuel is exposed to catalytic metals, such as copper, in the fuel system piping.[5-7] Degradation process can change fuel composition and properties until they no longer meet the established specifications as expected. When the altered property is not recoverable, i.e., cannot fall back within specification limits through filtering procedures, draining, etc., the fuel is rendered unserviceable for use in aircraft. Examples of parameters that are not recoverable and may cause QAV-5 to be unsuitable for aircraft replenishment gum test and jet fuel thermal oxidation test (JFTOT).

Actual gum test measures the amount of evaporation residues (gum) of an aviation fuel.[8] Gum is a mixture of high molecular weight compounds rich in oxygen, in higher concentrations than the indigenous heteroatomic compounds in fuel. Its solubility in fuel is, thus, limited

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and, when exceeded, these compounds precipitate and can adhere to the walls of the system, contributing to formation of varnishes or lacquer in hot spots.[9,10]

JFTOT measures the tendency of a jet fuel to generate deposits and is therefore an indicative of fuel thermal stability. JFTOT simulates the conditions in aircraft turbine and thus enables to observe whether jet fuel performance is acceptable in the most extreme thermal conditions of its application, since jet fuels act not only in aircraft propulsion but also as a coolant for various aircraft systems, by absorbing heat from hydraulic, lubrication and electrical systems.[5,11]

An envisaged alternative for reusing QAV-5 that can no longer replenish aircrafts is to blend it with Brazilian marine gasoil (ODM), the main fuel employed for propulsion of Brazilian Navy fleet, that has a similar specification to international ISO-F-DMA.[12] QAV-5/ODM blend would subsequently be burned in diesel engines of Navy ships. However, some of the differences between QAV-5 and ODM could negatively impact the use of that blend in marine engines.

Some of the key differences between QAV-5 and ODM are viscosity, specific gravity, cetane index and lubricity. The lower viscosity of jet fuels, compared to marine gasoil, can result in accelerated wear of diesel fuel components and internal leakage, especially in high pressure regions of fuel pumps and injector nozzles of diesel engines. Leakages, in turn, can lead to engine power loss.[13,14] QAV-5 also has lower specific gravity than ODM, which can lead to higher fuel consumption in engines, as the volume of fuel to be injected in combustion provides less mass. Cetane index is not a property measured for QAV-5, by specification. However, in a previous research,[14] cetane indexes were calculated for 10 samples of JP-5 and 20% of them exhibited results that fall below ODM specification limit. Lower cetane indexes lead to longer ignition delays, resulting in higher peak pressures when combustion occurs, which in turn can lead to durability problems in engines.[14] Jet fuels also provide less lubricity than marine gasoil, which can negatively affect diesel engines and cause accelerated wear in some components of the diesel system, such as pumps and fuel lubricated injectors.[13,14] Korres *et al.*[15] studied the use of blends of biodiesel and aviation kerosene (JP-5) in marine diesel oil. The authors reported that the addition of JP-5 reduced lubricity and increased the cetane number.

Lubricity is measured by high-frequency reciprocating rig (HFRR) test (ASTM D6079), by standard.[16,17] However, high cost and imprecision of mechanical lubricity measurement methods such as HFRR led to the development of an alternative method of monitoring lubricity called fuel lubricity haze test (FLHT). This chemical and optical method consists of the extraction of surfactant materials from the fuel, by adding a NaOH solution to the sample, with consequent formation of an emulsion. The turbidity of the emulsion is measured in a portable turbidimeter and the reading, in nephelometric turbidity units (NTU), is used as an indicator of fuel lubricity: higher lubricity fuels have more surfactants and, therefore, greater amount of emulsion formed and higher turbidity values.[18] Thus, QAV-5 is expected to provide lower turbidity values than ODM.

Not only these key differences must be taken into account when considering the use of QAV-5 in diesel engines, but also the degradation state of the jet fuel to be blended with ODM, which can alter its properties. Therefore, such blend must be analyzed in order to identify whether it is, in fact, suitable for use in marine engines, as well as the levels of QAV-5 that can be added to ODM in order to keep the mixture within ODM specification.

Experimental

Materials

Both QAV-5 and ODM were supplied by Brazilian Navy. A copper-nickel (CuNi) 90/10 alloy tube was also supplied by Brazilian Navy and cut into 70 coupons with approximate dimensions of 49.30 cm × 17.65 cm × 2.10 cm. A 480 liters explosion proof storage oven, with 3 shelves, was employed in the accelerated aging of QAV-5 samples.

For fuel lubricity haze test, a 0.2 mol L^{-1} NaOH (Merck 98%) solution was prepared in water and methanol (Tedia HPLC grade) (50/50) solvent. For this extraction solution, 97% pure NaOH, 99.9% pure distilled water and filtered methanol were used.

A portable turbidimeter with datalogger and Universal Serial Bus (USB) interface, with measurement range from 0 to 1100 NTU, was employed for turbidity readings.

Procedure

QAV-5 was distributed in 35 borosilicate glass flasks with 1-liter capacity each.

CuNi coupons were subjected to surface treatment, that consisted of abrading with 400 grit sandpaper, followed by abrading with 600 grit sandpaper and subsequent acetone wash. After drying, 2 CuNi coupons were inserted into each borosilicate glass flask, hung by nylon thread, so that they were completely submerged in the jet fuel and did not touch one another or the surfaces of the flask.

Flasks were stored in the explosion proof oven, which was thermostatically controlled to maintain a temperature of 50 °C, for 16 weeks. Every 4 weeks, 7 samples of QAV-5 were removed from the oven and mixed, and the mixture was analyzed for thermal oxidation stability by JFTOT (ASTM D3241)[5] and gum content by actual gum test (ASTM D381).[8]

QAV-5 was then used in the preparation of blends with ODM, according to proportions observed in Table 1.

Table 1. ODM and QAV-5 volumetric contents in each blend

Fuel/blend	P1	P2	P3	P4	P5
ODM / %	100	75	50	25	0
QAV-5 / %	0	25	50	75	100

P1 was only analyzed for zero-week data (t_0). P2, P3, P4 and P5 were analyzed in t_0 and then at 4 weeks intervals (t_1 = 4 weeks, t_2 = 8 weeks, t_3 = 12 weeks and t_4 = 16 weeks). ODM: marine diesel oil; QAV-5: jet fuel for Brazilian Navy.

Samples P1, P2, P3, P4 and P5 were analyzed in duplicate for viscosity (ASTM D 445), specific gravity (ASTM D1298/ASTM D4052), cetane index (ASTM D4737) and lubricity (FLHT).[18-22]

FLHT was performed by transferring 12 mL of fuel sample and 2 mL of NaOH (Merck 99%) extraction solution to a 15 mL turbidimeter glass vial. The mixture was manually shaken for 1 min with strokes about 25 cm long, at an approximate repetition rate of 1 s *per* shake. The vial was then externally cleaned and left on bench for a wait time of 10 min. Finally, the vial was inserted into the turbidimeter for turbidity reading.

Results and Discussion

Accelerated aging

The test measures the high-temperature stability of jet fuel, specifically focusing on its thermal oxidation behavior. Jet fuel is pumped through a heated stainless steel tube to simulate turbine engine conditions. The goal is to assess the formation of deposits on a heated aluminum tube, which can indicate how much the fuel deteriorates when exposed to high temperatures.

Oxidation process in QAV-5 was assessed during the 16-week period of accelerated aging in the storage oven, which corresponds to approximately 32 months storage at ambient temperature (20 °C).[22-26] During this period, fuel samples got gradually darker. Color change from original transparent to dark yellow was a visible sign of oxidation of the jet fuel, accelerated by both heat and contact with CuNi coupons that simulated the exposure of QAV-5 to CuNi 90/10 piping in Navy ships. Degraded, out of specification limits QAV-5 was obtained at 16 weeks (t_4), as can be seen in JFTOT and actual gum test results (Table 2).

Actual gum tends to increase with fuel storage time, as expected, except for t_3 sample. In fact, both actual gum and JFTOT results from t_3 are notably characteristic of a less degraded fuel than those from t_1 and t_2, indicating that QAV-5 t_3 did not undergo oxidation as expected. Therefore, the question arises concerning the homogeneity of heat distribution among oven shelves, since all QAV-5 samples used to produce the QAV-5 t_3 mixture were collected from flasks from the same shelf (middle shelf). Another hypothesis for the unexpected results for t_3 is a possible difference in the composition of QAV-5 samples used to prepare the t_3 mixture, such as a lower content of heteroatomic compounds or trace metals that would catalyze the oxidation reactions. The uneven heat distribution hypothesis is, however, more likely, since it would be a coincidence that QAV-5 from all flasks removed in t_3 presented the same chemical irregularity. This hypothesis is also strongly corroborated by the fact that even when the oven was turned off at the end of the 16-week period, the only remaining flask on the middle shelf remained colorless, showing no signs of an oxidative process. On the other hand, samples from the lower shelf were already yellowish after an 8-week period (t_2).

Thermal stability was remarkably degraded in t_4, as can be noted by JFTOT results. Deposit with more intense coloration than the threshold color standard, in addition to multicolored ("peacock") deposit formation on the heating tube indicate that the fuel will no longer have an unacceptable performance in the thermal conditions of the turbine. In this oxidation state, QAV-5 thermal stability is

Table 2. JFTOT and actual gum test results for QAV-5 samples removed from storage oven in t_0, t_1, t_2, t_3 and t_4

Property	Limit[a]	t_0	t_1	t_2	t_3	t_4
Actual gum (max.) / (mg *per* 100 mL)	7	0.6	3.4	4.2	2.6	16.5
JFTOT						
Pressure drop (max.) / mmHg	25	0.02	0.00	0.19	0.00	0.07
Tube deposit code	< 3	< 1	< 1	< 1	< 1	> 4 P[b]

[a]Limits as *per* Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP) Resolution 895/2022.[1] [b]Code P represents "peacock", a multicolor, rainbow-like heater tube deposit that does not match standard deposit color codes.[11] JFTOT: jet fuel thermal oxidation test.

compromised and the jet fuel can no longer fulfill its role as coolant for aircraft systems. Thus, QAV-5 t_4 cannot be used in aircraft replenishment service, by both JFTOT and actual gum criteria.

QAV-5 only failed actual gum and JFTOT criteria after a 16-week accelerated aging period, corresponding to a 32-month storage at ambient temperature. However, as above discussed, samples from the 12-week withdrawal did not degrade at the same rate as the others. Thus, it would be possible that QAV-5 would have failed specification limits earlier, in t_3, where all samples had the same oxidation rate.

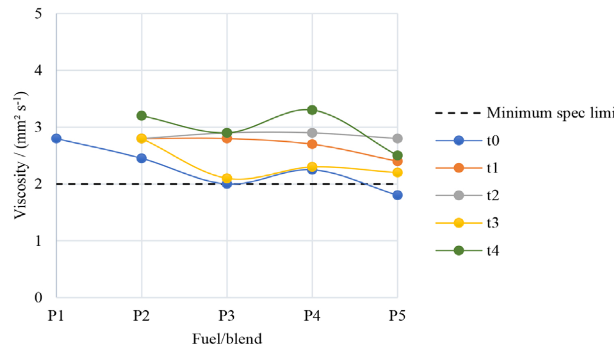

Figure 1. P1, P2, P3, P4 and P5 viscosities in each sampling period.

Analysis of blends

Results of QAV-5 and QAV-5/ODM blends are compared with ODM property limits specified in Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP) Technical Regulation 05/2010[16] and proposed pass/fail criterion for lubricity specified in technical report "Development of a Fuel Lubricity Haze Test (FLHT) for Naval Applications",[18] as shown in Table 3.

Viscosity

In general, a downward trend in viscosity is observed as QAV-5 content increases, so that pure QAV-5 result in zero-week analysis (P5 t_0) is below the minimum limit specified for ODM (Figure 1). QAV-5 low viscosity may have adverse effects on diesel engines, given that their internal components are designed with less stringent spacing tolerances compared to aircraft turbine engines, making their moving parts more susceptible to surface contact. Hence, continuous use of a low lubricity fuel, such as QAV-5, could cause accelerated wear in some of the engine components that are fuel lubricated. It can also cause engine hot start problems, as well as internal leaks in high pressure regions of systems designed to operate with gasoil, with consequent engine power loss.

However, viscosity of fuels and their blends tend to increase with QAV-5 aging. An increase in viscosity is a typical change noted during the aging of fuels, whether they are conventional petroleum-based fuels or biofuels, caused by both the loss of lighter components by vaporization and the formation of compounds with longer and more complex chains, as a result from the oxidative process.[27-29] Such an increase in viscosity favors blends with high QAV-5 content and even pure jet fuel, since QAV-5 (P5) viscosity falls within the acceptable range only after aging.

Notably, t_3 curve was an exception to the tendency of viscosity increase over time. Although this curve starts close to t_1 and t_2 curves for the blend with highest ODM content (P2), it approaches t_0 curve as QAV-5 is added to the mixture. This is a significant indication that QAV-5 removed from the oven in t_3 underwent a different aging rate compared to the rest of the samples. Therefore, JFTOT and actual gum test results are reinforced, as well as the hypothesis for their cause.

García-Contreras *et al*.[30] observed in their work using biodiesel that the incorporation of biodiesel increased the viscosity of fuel blends, though the effect was not linear with the percentage of biodiesel added. For example, a 15% biodiesel addition increased the viscosity of Jet A1 blends by 21% and synthetic paraffinic kerosene (SPK) blends by 32%. Despite the absence of aromatic compounds in SPK, its blends have higher viscosity than Jet A1 blends. This is attributed to longer hydrocarbon chains and large-branched alkanes in SPK, which contribute to its higher viscosity.

Table 3. Specification limits for ODM in service

Characteristic	Limit	Method[a]
Viscosity at 40 ºC / (mm^2 s^{-1}) (cSt)	2.0-6.0	ASTM D 445[19]
Specific gravity at 20 °C (max.) / (kg m^{-3})	876.8	ASTM D1298 / D4052[20]
Calculated cetane index / min	40	ASTM D4737[22]
Lubricity (max.) / µm	30[b]	FLHT

[a]Limits for viscosity, specific gravity calculated cetane index are specified in ANP Technical Regulation 05/2010.[16] Limit for lubricity is specified in technical report "Development of a Fuel Lubricity Haze Test (FLHT) for Naval Applications".[18] [b]Pass/fail limit for lubricity, by the FLHT method with manual agitation, would be around 20 to 30 NTU.[18] Therefore, the more conservative value of 30 NTU was adopted as minimum limit. FLHT: fuel haze lubricity test.

Specific gravity

Fuel specific gravity notably decreases as QAV-5 is added to the blend (Figure 2). ODM maximum specification limit of 876.8 kg m^{-3} was not even represented in Figure 2, since the obtained results are far below it. However, even though there is not a minimum specification limit for this property, low specific gravity fuels can lead to higher fuel consumption in diesel engines. Pure QAV-5 has specific gravity up to 3% lower than ODMs. Thus, it is advisable to monitor fuel consumption when using QAV-5/ODM blends, especially those with higher jet fuel content.

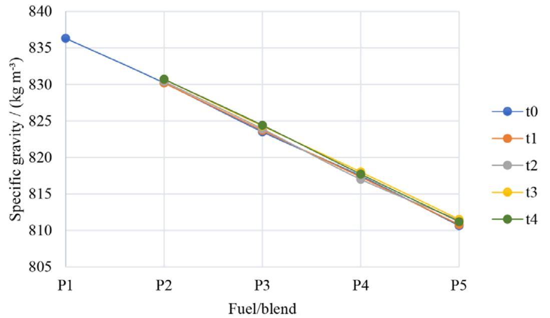

Figure 2. P1, P2, P3, P4 and P5 specific gravities, in each sampling period.

As opposed to viscosity, no visible trend was observed for specific gravity changes over storage time of QAV-5. In fact, results for QAV-5 and for each blend are almost unchanged through the jet fuel aging period.

Cetane index

Cetane index also decreased with increasing QAV-5 content (Figure 3), except for P3 t_4 and P4 t_4, which remained practically identical, with a 0.2% difference. Despite QAV-5 is not assessed for this parameter by specification, its cetane index was expected to be lower than ODMs, based on a previous study[14] with a similar military jet fuel JP-5. Cetane index of QAV-5 (P5) is, on average, 13% lower than that of ODM, considering results of all samples removed from the storage oven. The cetane index decrease caused by the addition of QAV-5 to ODM may lead to longer ignition delays in engines, thus impacting ignition quality and engine durability. It might also reduce acceleration and engine power, especially at full throttle and in engines with higher injection pressures.[14]

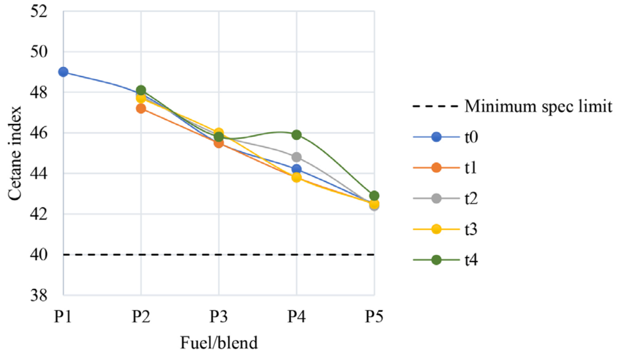

Figure 3. P1, P2, P3, P4 and P5 cetane indexes, in each sampling period.

However, all results, including pure QAV-5, were still above the minimum limit required for ODM. Thus, regarding the quality of ignition, problems are not expected in diesel systems when using QAV-5, even in this state of degradation, instead of ODM.

Finally, as observed for specific gravity, there was also no clear trend of cetane index change as a function of aging time of QAV-5, so that the degradation of jet fuel in this period, corresponding to a 32-month storage at ambient temperature, had no significant impact on this property.

Lubricity

As expected, lubricity also decreases as QAV-5 content in the blend increases, to the point that pure QAV-5, in any oxidation state, fails lubricity pass/fail limit (Figure 4). QAV-5 reduced sulfur content, compared to ODMs, contributes greatly for the lubricity decrease in the blend, since sulfur compounds provide lubricating properties to the fuel. Since pass/fail limit for lubricity, by FLHT method with manual agitation, would be around 20 to 30 NTU,[18] the more conservative value of 30 NTU was used as minimum limit in the graph. However, regardless of whether 20 or 30 NTU is adopted as minimum limit, all results pass the lubricity requirement, except for pure QAV-5.

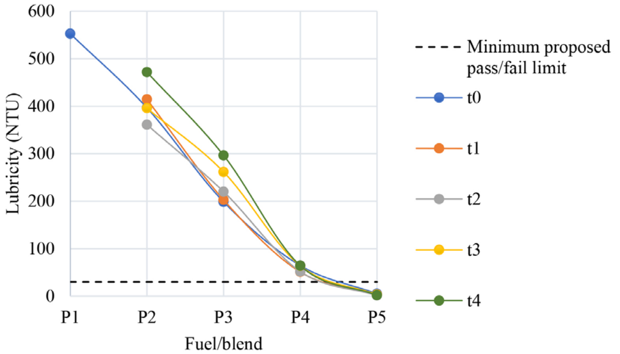

Figure 4. P1, P2, P3, P4 and P5 lubricities, in each sampling period.

Results are favorable to QAV-5/ODM blends, as it is possible to add substantial amounts of jet fuel to diesel while retaining the blend lubricity within the desirable limit: considering the average lubricities of P4 and P5, QAV-5 content in the blend could be up to approximately 88%. However, although FLHT has a good correlation with mechanical methods, it is not the required test by standard to verify the lubricity of Brazilian marine gasoil. In order to confirm the suitability of the samples with regard to lubricity, it would be necessary to conduct an HFRR lubricity test, especially in P4 and P5 samples and their intermediate blends, considering that the failure limit will be between 75 and 100% QAV-5 content in the fuel.

Finally, QAV-5 degradation state did not directly impact the lubricity of the blends. Although t_4 curve begins at higher lubricity values, this difference decreases as QAV-5 content in the mixture increases to the point where pure QAV-5 (P5 t_4) has lower lubricity than the same jet fuel in less degraded states. Therefore, it appears that QAV-5 degradation was not responsible for the lubricity increase observed in P2 t_4 and P3 t_4.

Anastopoulos *et al.*[31] examined the impact of monocarboxylic acid esters on the lubricity of JP-8 military aviation fuel, with the following conclusions: JP-8 lacks sufficient lubrication when used in army ground vehicles, risking fuel pump damage. Small amounts of esters (800-1,000 ppm) improved lubricity, reducing wear scar diameter to acceptable limits, but further ester additions offered no significant benefit. Studies related[32,33] to aviation kerosene and marine diesel oil are related to the addition of biofuels, such as biodiesel and ethanol, but are not related to the reuse of off-specification fuels.

Conclusions

Accelerated oxidation of high flash point, special jet fuel for Brazilian Navy (QAV-5) was conducted in an explosion proof storage oven for 16 weeks at 50 °C, simulating fuel storage for 32 months at ambient temperature (20 °C) and was effective in jet fuel accelerated aging. Based on JFTOT and actual gum test results, performed every 4 weeks, it was confirmed that QAV-5 underwent degradation during storage. By the end of the period that corresponded to a 32-month ambient storage, the fuel had compromised thermal stability and high generation of gum, therefore becoming unserviceable for use in aircraft. Results referring to the removal of QAV-5 samples after 12 weeks of accelerated aging, however, were outside fuel deterioration trend. That raises the likely hypothesis of an uneven heat distribution among oven shelves, which could have led QAV-5 samples from this specific withdrawal (all from the same oven shelf) to undergo oxidation at a different rate compared to other samples. Therefore, although QAV-5 only failed to meet jet fuel specification limits at the end of the full storage period, it is possible that it would have been out of specification earlier, in the 12-week withdrawal, if such samples had degraded at the same rate as the others.

As for the impact of the addition of QAV-5 to ODM, a decrease in results of all analyzed properties was observed: viscosity, specific gravity, cetane index and lubricity. However, viscosity of QAV-5 tends to increase as the fuel ages, so this trend can be reversed and, at a given state of jet fuel degradation, blends with QAV-5 have an even higher viscosity than pure ODM. As for the other properties analyzed in this study, there was no visible change on specific gravity, cetane index or lubricity as a function of QAV-5 oxidation state.

Based on the results presented in this study, it is possible to use oxidated, out of specification QAV-5 in blends with ODM, to be burned in diesel engines of Brazilian Navy ships. Pure QAV-5, however, has very low lubricity and does not meet ODM specification. QAV-5 viscosity might also fall below ODM minimum requisite, especially for jet fuel that has not undergone significant oxidation process. Thus, in case of diesel engines for which the employ of jet fuel is not expressly allowed, it is not advisable to use pure QAV-5. Concerning viscosity, specific gravity, cetane index and lubricity, QAV-5/ODM blends with up to 88% (v/v) QAV-5 content could be used in diesel engines without damaging fuel system, since they remain within ODM specification limits. However, it must be emphasized that lubricity was measured by FLHT in this study, meanwhile ODM specification requires lubricity measurement by mechanical method HFRR. Therefore, as future studies, it would be advisable to investigate lubricities of QAV-5/ODM blends with QAV-5 volumetric content above 75% by the standard HFRR test, in order to assure the maximum QAV-5 content that can be added to ODM without compromising the lubricity of the blend.

Finally, although there is not a minimum limit for ODM specific gravity by standard, the noted decrease in this property as QAV-5 content increases in the blends may result in elevated fuel consumption in diesel engines. Hence, monitoring fuel consumption is recommended when utilizing QAV-5/ODM blends, particularly those containing a greater proportion of jet fuel.

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