



Suitability of a radical based method for assessment of jet fuel antioxidant capacity and projected storage stability



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HIGHLIGHTS

- Jet fuel storage stability test.
- DPPH assay of antioxidant species in jet fuels.
- DPPH assessed for feasibility as oxidative indicator for fuels.
- Comparison with known, established indicators of oxidative stability.
- DPPH response to fuels of known provenance correlated with phenolic content.

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ABSTRACT

Jet fuel stability is an important fuel property for management of fuel in storage. A method for predicting jet fuel stability, based on the colourimetric reaction of the stable free radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) has been examined in this work. A range of jet fuels of known and unknown refining history, including a range of antioxidant compounds have been examined using the DPPH assay with mixed results. It was found that the DPPH technique responds predictably with a range of phenolic species however was less predictable with jet fuels of unknown provenance. Little to no correlation was observed when comparing unknown fuels storage stabilities based on oxidative and peroxide formation tests against the DPPH assay, however a good correlation was observed for fuels of known refining history for these same storage stability tests. The wide variation of results may in part be due to the very complex reaction mechanisms of DPPH with species in the fuels and due to the inherent chemical complexity of middle distillate fuels that may have undergone ageing reactions in storage prior testing with the DPPH assay.

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1. Introduction

Oxidative stability is an important performance characteristic of jet fuels. Jet fuel stability can be defined in a number of ways including resistance to the formation of hydroperoxides, rate of reaction with oxygen, and resistance to sediment formation [1–3]. As jet fuels have historically been relatively stable in storage, no mandatory tests are required in most fuel specifications. How-

ever, jet fuel thermal stability can be measured by a range of assessment techniques such as ASTM D3241 Thermal Oxidation Stability of Aviation Turbine Fuels and ASTM D7739 Thermal Oxidative Stability Measurement via Quartz Crystal Microbalance. These two thermal stability techniques are useful in quantifying the sediment formation from fuels undergoing thermal stress under controlled conditions but may not reflect a fuel's projected stability under ambient storage conditions. Methods developed to assist with predicting storage stability have included a low pressure reactor technique (LPR) which measures hydroperoxide formation under low temperature stressing conditions [4,5]. Another method gaining wider use is ASTM D7545 Oxidation Stability of Middle Distillate Fuels – Rapid Small Scale Oxidation Test (RSSOT) and whilst more utilised for diesel and biodiesel blend stability, may offer some insights into jet fuel stability

Abbreviations: AO, antioxidant; DPPH, 2,2-diphenyl-1-picrylhydrazyl; SPK, synthetic paraffinic kerosene; IPK, synthetic iso-paraffinic kerosene; jet, fuel thermal oxidation test; QCM, quartz crystal microbalance; LPR, low pressure reactor; RSSOT, rapid small scale oxidation test.

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[6,7]. ASTM D4625 Standard Test Method for Middle Distillate Fuel Storage Stability at 43 °C is a method for assessment of sediment formation in fuels, however is often not favoured due to the long test times for ageing the fuels.

Jet fuels may contain compounds that influence their oxidative stability. These compounds include heteroatoms containing O, S, N and specifically phenolic compounds that are reported to provide a natural antioxidant capacity [8–10]. It has been reported that heteroatoms containing S and N may tend to increase sediment formation in storage [1,11], so compounds that may improve a fuel's resistance to oxidation may also promote sediment formation [12,13]. When a fuel is hydroprocessed, heteroatoms are removed and compounds that act as natural inhibitors are lost. These fuels may require the addition of a synthetic antioxidant additive, usually hindered phenols added in the 10 to 30 mg/L range.

To expand the range of tools available to predict fuel storage stability a technique for stability assessment widely used in the food, flavour, biological and biofuels industries was examined. This technique involves the use of the stable radical 2,2-diphenyl-1-picrylhydrazyl (DPPH) to evaluate a compounds antioxidative activity or anti-radical efficiency [14–20]. Irreversible oxidation of the DPPH radical and pairing of the lone electron shift the absorption band from deep violet at 520 nm, to colourless, which can be monitored using ultraviolet–visible (UV–Vis) spectrophotometry.

Antioxidant determinations using DPPH have successfully been used to quantify the antioxidant capacity of a range of compounds including phenolic species and hindered phenols similar to those used as antioxidants in hydrocarbon fuels, [21] and also for phenolic compounds found in or added to lipid oils [22,23]. The DPPH assay has also found use in the evaluation of natural antioxidants such as curcumin, β -carotene and α -tocopherol for use with biodiesel [24,25]. Other compound types including amines [26] and some sulfur species have been reported to provide antioxidant protection to hydrocarbon fuels.

Whilst assays using DPPH to measure antioxidant capacity have been examined widely, there are some recognised limitations of the DPPH assay. Its response is known to be influenced by a range of properties [27,28] including reaction solvent, pH, temperature, reactant concentration and the type of reactant mechanism for interacting with the DPPH molecule. Many previous studies have been undertaken in aqueous and polar solvents with fewer data available on non-aqueous systems such as those examined in this experiment. Also the DPPH molecule can be reduced by a range of materials that are not antioxidants, such as H_2O_2 .

Approaches for using the DPPH reaction to quantify a material's anti-radical efficiency are varied. These include calculating the EC_{50} parameter where the substrate concentration to produce a 50% reduction in DPPH is calculated [14,16,29,30]. Alternatively, DPPH can be measured over the course of the reaction until such time that it reaches a steady state and the colour stabilises. Finally, time-based methods have also been used reporting the remaining DPPH concentration after a fixed time such as 15, 30 and 120 min [31–33].

This paper examines the suitability of DPPH as an assessment of the antioxidant capacity of a range of hydrocarbon fuels including fuels of both known and unknown refining history. The results are also compared against other stability assessment techniques such as oxygen depletion rates and peroxide formation.

2. Materials and methods

2.1. Fuels

2.1.1. Fuels of known processing history

Five fuels with known fuel finishing process, antioxidant and sulfur contents were examined. Three of these were conventional,

crude oil-derived fuels, each finished with a different refinery process. These will be henceforth referred to as straight run, hydroprocessed, and merox processed jet fuels. Two of the fuels were synthetic blending components meeting ASTM D7566 Standard Specification for Aviation Turbine Fuel Containing Synthesized Hydrocarbons, identified as a biologically derived synthetic paraffinic kerosene (SPK) and a high temperature hydroprocessed isoparaffinic kerosene (IPK). These will be referred to in the rest of the text as Bio-SPK and HT-IPK, respectively.

2.1.2. Fuels of unknown refining history

Thirteen jet fuel samples numbered 147–161 were taken from in-service military bases and all meet the DEF(AUST) 5240 Aviation Turbine Fuel (Military Grades F-34, F-37 and F-44) specification. All of these fuels contained the military additive package consisting of fuel system icing inhibitor and a lubricity additive. As the refining history of these fuels was unknown they were further characterised by a commercial laboratory to provide information on properties that may impact fuel stability. Total sulfur was measured using ASTM D5453, existent gum using IP540 and total acidity using ASTM D3242. The BHT was quantified using an in-house gas chromatographic - mass spectrometer technique.

2.2. Reagents and standards

2.2.1. DPPH

2,2-Diphenyl-1-picrylhydrazyl was purchased from Sigma Aldrich (Castle Hill, NSW, Australia). DPPH solution was prepared by weighing 0.0501 g of DPPH into 1 litre of toluene in a calibrated volumetric flask. This solution was stored in a fridge and the same batch was used throughout the experimental program. Toluene was selected as a solvent to ensure solubility of all reactants.

2.2.2. Antioxidant-doped solutions

Solutions of 17 different antioxidant compounds or mixtures were prepared at concentrations of approximately 500 mg/L. This is well above the specified 17.2–24.0 mg/L required in the MIL-DTL-83133 turbine fuel specification [24]. This high antioxidant concentration was used to assist with discriminating between additive responses to the DPPH radical. All antioxidant compounds examined were synthetic phenols with the exception of two aryl amines, N-phenyl naphthylamine, which is commonly used in turbine engine oils and diphenylamine which was included as it is often used as a rapidly oxidising standard in antioxidant studies.

2.3. Ultraviolet–visible spectrophotometry

Spectrophotometric measurements were performed at 520 nm using Varian CARY Bio UV–visible spectrophotometer using the Cary WinUV kinetic software with a sampling frequency of 1 min. Cuvettes were CARY 7Q rectangular lidded quartz cuvettes. The cuvettes were fitted with a Starna 6 mm \times 3 mm magnetic stir bar, operated by a Starna Spinette electronic cell stirrer. All tests were performed by first adding 3 mL of pre-prepared 50 ppm DPPH solution to the cuvette, and then adding 100 μ L of test sample. The absorbance at 520 nm was then monitored for 120 min with continuous stirring of the sample. Here we have chosen to report both a percentage depletion and time-based approach, where the time to reach a 10% loss of DPPH (T90%) and percentage of DPPH remaining after 120 min to characterise fuel reaction with the DPPH radical have each been quantified.

2.4. Low pressure reactor and peroxide number

The five fuels of known refining history were stressed and peroxide content measured based on a process described by Pande

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