



## Full Length Article

# Characteristics and stability of biofuels used as drop-in replacement for NATO marine diesel

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## ABSTRACT

Catalytic hydrothermal conversion diesel (CHCD-76), synthesized isoparaffin (SIP-76), and hydroprocessed renewable diesel (HRD-76) have been produced in sufficient quantity and supplied to the U.S. Navy for blending with traditional marine diesel NATO F-76. The present work investigates the storage and oxidation stabilities of DSH-76, CHCD-76, and their blends with F-76. Chemical composition and physicochemical properties of these two biofuels, including viscosity, density, peroxide value, heat of combustion, acid number, and phase behavior, were determined using required ASTM methods. ASTM D4625 and D5304 methods were employed to investigate the long-term storage stability of these two biofuels and their blends with F-76. ASTM D5304 method was also modified to investigate the oxidation process of these fuel samples. In addition, ASTM D2274 tests were conducted to investigate oxidation stability of the neat and blended fuel samples. The influence of long-term storage and oxidation on fuel physicochemical properties was investigated based on ASTM methods. SIP-76 and CHCD-76 were found have superior storage and oxidation stability in comparison with petroleum F-76. This is also the first report on storage and oxidation stability of SIP-76 and CHCD-76.

## 1. Introduction

Recent interest in alternative transportation fuels has been driven by the finite nature of crude oil reserves and climate change resulting from the combustion of fossil fuels. Biofuels produced from renewable resources have been proposed as a potential solution to reduce net carbon emission and to improve energy security. In 2016, the renewable share of energy consumption in the United States reached 10.5%, the largest renewable share since the 1930s [1], and the energy produced from biofuel increased approximately 3 times from 755 Trillion KJ in 2006 to 2400 Trillion KJ in 2017 [2]. The US Navy is also interested in alternative fuels for blending with marine diesel NATO F-76 in order to decrease reliance on fossil resources and increase energy security. Alternative fuels are being sought as drop-in replacements, requiring no modification to existing equipment and fuel handling and transportation systems. In addition, the shipboard environment and mixed fuel-seawater ballasting practices on Navy ships present unique challenges for preserving fuel quality [3].

Non-ester renewable fuel (NERF) is a class of biofuels comprising pure hydrocarbons that are indistinguishable from their petroleum counterparts. NERFs have many advantages over bioethanol and biodiesel, e.g. higher energy content, better low temperature quality, and superior stability and material compatibility [4]. NERFs are also

interchangeable with petroleum diesel in the existing fuel distribution and diesel engine infrastructure. As such, NERFs are more likely to meet the specifications of alternative fuels. NERFs, such as hydroprocessed renewable diesel (HRD-76), catalytic hydrothermal conversion diesel (CHCD-76), and synthesized isoparaffin (SIP-76), also known as direct sugar to hydrocarbon (DSH-76), have been produced in sufficient quantity for testing by the US Navy as drop-in replacement for NATO F-76.

HRD-76 is produced by hydroprocessing oils derived from algae and animal fat [5], and this process generates a mixture of saturated C<sub>15</sub>–C<sub>18</sub> linear and branched alkanes [6–8]. The reaction pathway during hydroprocessing involves two major steps: (i) saturation of the double bonds of the triglycerides and breaking the saturated triglycerides to fatty acids; and (ii) conversion of fatty acids into alkanes through hydrogenation or decarboxylation processes [7,9]. Similar to HRD-76, CHCD-76 is produced by hydrothermal processing and the feedstock is non-food plant oil [4,10–11]. In this process, the plant oil is first converted to stable intermediate oil products using water, and the intermediate oils are then hydroprocessed with catalysts to generate biofuel. The biofuels are further distilled to obtain diesel, jet fuel, naphtha, and liquefied petroleum gas. In contrast to HRD-76 and CHCD-76, SIP-76 is a sugarcane-based renewable fuel produced by fermentation [12–14]. The conversion process begins with the

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fermentation of sugar with engineered yeast to produce isoprenoids  $\beta$ -farnesene, a  $C_{15}$  unsaturated hydrocarbon. The fermentation can be conducted via the mevalonate or deoxyxulose phosphate metabolic pathways [13], in which farnesyl pyrophosphate, an intermediate, is formed and transformed to farnesene via the farnesane synthase enzyme. The farnesene was then separated from the fermentation broth and hydroprocessed to produce the final product farnesane.

Although a blend of HRD-76, CHCD-76, SIP-76, and conventional F-76 has already been used to power Navy surface ships [15], the physicochemical properties and storage and oxidation stability of CHCD-76, SIP-76, and their blends with F-76 haven't been thoroughly investigated. In the present study, the physicochemical properties and chemical composition of CHCD-76, SIP-76, and their blends with F-76 were measured. Two American Society of Testing and Materials (ASTM) methods, i.e. ASTM D4625 [16] and ASTM D5304 [17], were used to investigate the storage stability of these fuel samples. ASTM D5304 was also modified to determine the oxygen consumption rate of fuels. ASTM D2274 testing [18] was conducted to study the fuel oxidation stability. Additionally, fuel properties, such as density, viscosity, peroxide value, heat of combustion and acid number, were also measured according to the ASTM methods after stressing the fuel samples.

## 2. Materials and methods

### 2.1. Materials

Petroleum F-76, SIP-76 and CHCD-76 were provided by the Naval Fuels and Lubricants Cross Function Team at Patuxent River, Maryland, United States (PAX River). The SIP-76 and CHCD-76 fuel lots were synthesized by Amyris Biotechnologies and Applied Research Associates, respectively. The petroleum F-76 was refined by CITGO Petroleum Corporation. The fuels were used as received, unless otherwise noted.

### 2.2. Physicochemical properties

The composition of SIP-76 and CHCD-76 was determined by gas chromatography/mass spectrometry (GC/MS). 1  $\mu$ L fuel samples were dissolved in 1.5 mL hexane and analyzed using a Bruker 436-GC gas chromatograph and SCION-MS select, single quadrupole mass spectrometer (Bruker Corp., Billerica, MA). The GC was equipped with an Agilent DB1701 column (low/mid polarity, 60 m, (14%-cyanopropyl-phenyl)-methylpolysiloxane) with a 15 m guard-column before the back flush valve and operated at a helium flow rate of 1.5 mL/min. Hydrocarbon reference standards purchased from AccuStandard (AccuStandard, New Haven, CT) and Sigma-Aldrich were used for chemical identification and composition determination. A LECO CHN628 (LECO Corp., St. Joseph, MI) was employed for the carbon, hydrogen, and nitrogen content determination of fuels samples. The furnace and afterburner temperature of the system was set at 950 and 850 °C, respectively. Approximately 60 mg of fuel sample was placed in a tin foil cup and then covered with  $\sim$ 300 mg Com-Aid ( $>$  99%  $Al_2O_3$ , purchased from LECO Corp., Part No. 501-427) and sealed. The H/C was calculated based on the carbon and hydrogen analysis results.

An Anton Paar SVM3000 Stabinger Viscometer (Anton Paar USA Inc., Ashland, VA) was used to measure the viscosity and density of neat and stressed fuel samples at temperatures according to the ASTM D7042 method [30]. The accuracy of the viscometer was tested with a certified viscosity standard oil (APN26, Paragon Scientific Limited, UK) and the measurement repeatability was  $\pm$  0.1% of reading for viscosity,  $\pm$  0.0002 g/cm<sup>3</sup> for density, and  $\pm$  0.005 °C for temperature. A Parr 6200 Isoperibol Calorimeter (Parr Instrument Company, Moline, IL) was used to measure the heat of combustion, i.e. heating value, based on the ASTM D4809 method [19]. The heat of combustion reported in this study is the high heating value (HHV). A Setaflash Series 8 closed cup flash point analyzer (model 82000-2 U) was used to

measure the flash point of fuel samples according to ASTM D3828 method (hot wire ignition). For each fuel sample, at least two measurements of flash point were taken using temperature ramping mode and one more measurement was conducted using flash/no flash mode to validate the data obtained. ASTM D3703 [20] and ASTM D974 [21] were employed to determine the peroxide value (PV) and acid number (AN) of fuels, respectively. PV is an indication of the quantity of oxidizing constituents present in the fuel samples that may influence various parameters, such as density and viscosity.

Differential scanning calorimetry (DSC) analyses were conducted using a TA Q2000 system (TA Instruments, New Castle, DE) equipped with an RCS90 temperature control which permits operation over the temperature range of  $-90$  to  $400$  °C. A Tzero low-mass, hermetically sealed pan (TA Instruments, Part No. 901684.901 (lids) and 901670.901 (pans)) was selected for analyses with a sample mass of 2–3 mg. A purge gas of ultra-high purity nitrogen with a flow rate of 50.00 mL/min was regulated by a mass flow controller. Cooling and heating scans for fuel samples were conducted with the following program: (1) equilibrate at 20 °C, cool at 5 °C/min to  $-90$  °C, and hold isothermally for 3 min; (2) heat at 5 °C/min to 20 °C, and hold isothermally for 3 min; (3) repeat step (1) and (2). The step (3), repeated cooling and heating scan, is conducted to ensure that the pan is well sealed and the curve is repeatable. The cooling scan was analyzed to determine the crystallization onset temperature (FO) and the crystallization peak temperature (FP), which reflect the low-temperature quality of fuels.

### 2.3. Storage stability

The ASTM D4625 [16] and D5304 [17] methods were employed to test the storage stability of SIP-76, CHCD-76 and their blends with F-76. ASTM D4625 [16] and D5304 [17] were developed to evaluate the storage stability of middle distillate petroleum fuel [22–25]. Following ASTM D4625 [16] fuels were stored at  $43 \pm 1$  °C for 24 weeks with samples analyzed after 0, 4, 8, 12, 16, 18, and 24 weeks to measure the amount of insolubles formed. For this method, one week of storage at 43 °C is roughly equivalent to a month of storage at normal ambient temperature, 21 °C [16]. The ASTM D5304 is an accelerated method compared with ASTM D4625. The storage stability of the fuel is evaluated after undergoing 16 h subjected to an oxygen atmosphere at 90 °C and 800 kPa. The 16 h test is expected to yield approximately the same amount of insolubles as 20 °C storage for 27 months under 101.325 kPa air pressure [17].

The total insolubles formed during the ASTM D4625 and D5304 tests include filterable and adherent insolubles – the filterable insolubles are solid particles formed during storage which can be removed by filtration and the adherent insolubles are gums formed during storage that remain tightly attached to the walls of the test vessel. Both test methods call for stressing the fuel followed by cooling for  $60 \pm 5$  min in the dark at room temperature. In all cases, the aged samples were filtered using two Whatman nylon membrane filters (47 mm diameter and 0.8  $\mu$ m pore size) to quantify filterable insolubles. Adherent insolubles were removed from the storage bottle with trisolvent (a mixture of equal mole of acetone, methanol, and toluene). The solvent was then evaporated at 160 °C to obtain the adherent insolubles. Military specification MIL-DTL-16884N (2014) identifies maximum allowable total insolubles of 3.0 mg/100 mL for NATO F-76 analyzed by ASTM D5304.

### 2.4. Oxidative stability

The ASTM D2274 [18] is an accelerated method developed to quantify the oxidation stability of distillate fuel oil [22–24]. This method requires an elevated temperature, 95 °C, and exposure to a continuous flow of pure oxygen, 3 L h<sup>-1</sup>. Similar to ASTM D4625 and D5304, the filterable and adherent insolubles formed were quantified

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