



Full Length Article

Extensive chemical characterization of a heavy fuel oil

V. Garaniya^{a,*}, D. McWilliam^b, L. Goldsworthy^a, M. Ghiji^c^a Australian Maritime College, University of Tasmania, Launceston, Australia^b School of Chemistry, University of Tasmania, Launceston, Australia^c Institute of Sustainable Industries and Liveable Cities, Victoria University, Victoria, Australia

ARTICLE INFO

Keywords:

Heavy fuel oil
 Characterization techniques
 Combustion modelling

ABSTRACT

This paper presents procedures for determining the fractions, chemical compositions and combustion characteristics of Heavy Fuel Oil (HFO). This chemical characterization is requisite for better prediction of thermodynamic behaviour of multicomponent fuel such as HFO which consist of thousands of different components. Detailed chemical and physical compositions, molecular weight range and mean molecular weight of individual fractions of fuel enable to use more advanced approaches such as continuous thermodynamics for simulation and modelling. Sequential elution solvent chromatography was used to separate a HFO into Saturates, Aromatics, Resins and Asphaltenes (SARA) as gas chromatographic analysis was unsatisfactory to reveal the overall composition of a HFO, due to the insufficient volatility in most of the heavy compounds. Subsequent mass spectrometric and elemental analysis showed a wide range of molecular weight distributions for the fractions. The results also indicate that the saturates fraction contains cyclic structures with aliphatic side chains while the aromatics fraction contains tetracyclic aromatic rings with aliphatic side chains. The degree of difference between the Thermo-Gravimetric Analysis (TGA) scans of the fractions in inert and oxidizing atmospheres observed at high temperatures also increases with the degree of functionality of the fractions due to the presumably greater extent of free radical chemistry occurring in an oxidizing environment. The Infrared spectra of the fractions are consistent with what would be expected from a consideration of the solvents used to elute them in column chromatography and supported the classification of the fractions.

1. Introduction

Maritime transport is the dominant form of transport because it is economical, energy efficient, emits fewer pollutants per tone-km of goods displacement and is regarded as the safest means of transport. It uses Heavy Fuel Oil (HFO) as the primary source of fuel, which is a blended mixture of the residue from vacuum distillation and a more volatile fuel (cutter stock) [1]. The residue has a high viscosity and before it can be used as fuel, cutter stock is blended with it to lower the viscosity, and to aid the combustion in marine compression ignition engines. Cutter stock may also have a high aromatic content but it has lower molecular weight than the residue [1]. Heavy fuel oil is highly aromatic and has a high carbon to hydrogen ratio. In the industry, HFO is also known as Bunker Fuel Oil (BFO) or Residual Fuel Oil (RFO) while some lighter forms are known as Intermediate Fuel Oil (IFO).

Current global environmental legislation and the steady increase in emission regulations have forced the transport industry to develop higher performing and more efficient engines [2–4]. The demand of modern on-road transport has forced oil refineries to produce more

lighter oil fractions (gasoline, diesel, etc.) and this greater demand together with advancements in petroleum refinery operations has had a direct impact on the quality of HFO. Subsequently, large marine engines are receiving more and more carbon-rich and higher aromatic content HFO. As a result of this poor quality fuel, engine problems are occurring [5] because aromatics are very stable and difficult to ignite. Some of the major issues are piston ring wear, cylinder liner scuffing and exhaust valve sticking [6]. The combustion process of this poor quality fuel in engines is very complex; it involves not only burning of volatile components but also burnout of coke residue. Although HFO is the most important source of fuel, because of difficulties in combined modelling of preferential evaporation and pyrolysis mathematically, to date very little effort has been made to model the behavior of such multicomponent fuels [7]. Limited research work has been found in the literature on evaporation of multicomponent fuels and most of this work is based on binary component mixtures or up to ten discrete components. This discrete component approach is inadequate in representing fuels such as HFO, which contains thousands of different components. An alternative approach is required to treat a multi-

* Corresponding author.

E-mail address: v.garaniya@utas.edu.au (V. Garaniya).

component fuel such as the continuous thermodynamics technique, which represents the fuel components as a series of multi-distribution Probability Density Functions rather than a series of discrete components. Hence it reduces computational simulation load compared to discrete component modelling without degradation of the prediction quality of the complex combustion. The present paper outlines a method of determining the chemical composition of HFO by separating the HFO into fractions that differ in their chemical composition and physical properties, and by analyzing each fraction. The chemical findings obtained from the separated fractions can be used in HFO combustion modelling including continuous thermodynamics.

The physical and chemical properties of fuels differ according to the location, depth, and age of the source of the crude oil. Chemical characterization of a multi-component fuel is an essential tool for understanding its behavior during combustion, as its combustion characteristics are directly related to its composition [8]. Heavy fuel oil is chemically very complex consisting of many different compounds. A complete characterization of a HFO is impractical if not impossible [9]. However, there are methods by which the overall composition can be determined by analysing and grouping similar components. Rahimi & Gentzis [9] have reported methods for separating HFO into different fractions based on solubility and adsorption properties. A commonly employed method of fractionating HFO into smaller fractions involves separation by column chromatography, firstly used by Jewell et al. [10], and a compound class characterization [11] commonly known as SARA, where SARA stands for Saturates, Aromatics, Resins and Asphaltenes (SARA) fractions. The saturates and the aromatics classes contain non-polar hydrocarbons. The resins fraction is the second least volatile fraction of HFO after the asphaltenes, while the asphaltenes have the highest molecular weight and polarity. The asphaltenes and resins fractions contain sulphur, nitrogen and oxygen in addition to carbon and hydrogen and are the polar components of the HFO. This polarity of the resins and asphaltenes is mainly responsible for their low volatility.

Often the asphaltenes fraction is initially precipitated from the HFO by treatment with a non-polar hydrocarbon solvent. The remaining fractions (saturates, aromatics and resins) commonly known as maltenes, are then separated by sequential elution solvent chromatography (SESC). In this technique, progressively more powerful solvents are employed to elute progressively more polar fractions from an adsorbent. A column filled with adsorbent media is employed, and a sample of maltenes is introduced at the top of the column. Different fractions of the maltenes are removed by passing different solvents through the column and collecting the eluent as it emerges from the column. Clearly, both the choice of solvents and adsorbent are important. Most researchers prefer to remove asphaltenes from the samples prior to chromatography because asphaltenes contain very polar compounds which are likely to be irreversibly adsorbed by the adsorbent. Once the fractions are separated, they can be analysed by various methods as outlined later in this paper. Many researchers such as Yasar et al. [12], Vazquez & Mansoori [13], and Farcasiu [14] have used silica gel as the adsorbent media for sequential elution solvent chromatography of petroleum. Liu et al. [15], Schiller & Mathlason [16] and Marquez et al. [17] used alumina while Burke et al. [18] have used glass beads. In addition to different adsorbent media, many different solvents have been used for the elution of the fractions. Summaries of the solvents used by various researchers for precipitation of asphaltenes from HFO and of the solvents and adsorbents used for SESC chromatography are given in Garaniya [7].

Elemental Analysis (EA) provides the molecular composition and estimates the heteroatom content of each separated fraction of HFO components [19]. With aid of this extensively used technique, intricate multi-component fuels such as crude oil and HFO can be characterized [20,21]. The structure of organic molecules [19], physical and chemical properties [22] of multi-component fuels can be investigated using Nuclear Magnetic Resonance (NMR) technique. Despite methods such

as gas chromatography and mass spectrometry, this technique enables to characterize high molecular weight components of HFO [23]. The results of NMR analysis enhance our knowledge about properties of heavy components which are playing a key role in the combustion process and subsequently the formation of emissions [24,25].

Moreover, in order to characterize the combustion features of HFO, Thermo-Gravimetric Analysis (TGA) can be conducted as the principal thermo-analytical technique [26–29] where the continuous physical and chemical changes of a sample are obtained and investigated. Pioneer study by Tadema [30] showed how TGA could reveal the thermodynamic behaviors of HFOs. Later on, a combined application of Differential Scanning Calorimetry (DSC) and TGA became a conventional approach for researchers [19,31]. Most recently, Fan et al. [32] and Elbaz et al. [19] carried out TGA to investigate the oxidation behavior and kinetics parameters of heavy fuel oil. Elbaz et al's results showed that the activation energy of high-temperature region (497–580 °C) is higher than that for low-temperature region (25–342 °C).

2. Experimental analyses

A sample of marine HFO was collected from the port of Sydney and New South Wales, Australia. All other chemicals used were standard laboratory chemicals and all solvents were purified by fractional distillation prior to their use. This precaution was taken to avoid contamination of the original sample by high boiling point impurities in the solvent, which could be concentrated on evaporation of the solvents after fractions were collected. Gas chromatography was used to check the quality of the solvents before and after fractional distillation.

2.1. Procedure

A flowchart of the experimental procedure used for HFO separation is shown in Fig. 1.

2.2. Precipitation of asphaltenes

The asphaltenes fraction was initially separated from the HFO because it can cause adverse effects on the adsorbent by becoming irreversibly adsorbed. Asphaltenes are also known as 'bad actors' in refineries as they promote coke and sludge formation as well as causing catalyst deactivation during the processes. As described in the literature [14,33], a 40:1 ratio of solvent to sample was used. An accurately weighed sample (2.557 g) of the HFO was mixed with 100 mL of purified n-pentane. This mixture (HFO + n-pentane) was stirred for 24 h at room temperature and allowed to settle for approximately 3 h. The precipitated asphaltenes fraction was separated by vacuum filtration through a 0.2 µm Nylon filter. The solvent was allowed to evaporate from the filter at room temperature in a vacuum desiccator for approximately 24 h and the weight of asphaltenes determined.

2.3. Separation of maltenes into Saturates, aromatics and resins

The maltenes in pentane solution was isolated from asphaltenes by vacuum filtration and collected as a filtrate as described above. During vacuum filtration, some solvent loss occurred and n-pentane was added to make up the volume of the solution of maltenes to 50 mL. 10 mL (20% by volume) from this solution was mixed with 15–20 g silica gel, which had been previously activated by heating for 24 h at 115 °C. Precautions were taken to ensure uniform mixing of the solution of maltenes with the silica gel by using a vacuum rotary evaporator to remove the solvent during the mixing of silica gel and maltenes over a period of approximately 3 h.

A glass column with an internal diameter of 2 cm and a height of 35 cm was used for the sequential elution solvent chromatography (SESC). The column was filled with a slurry of pre-activated silica gel

Download English Version:

<https://daneshyari.com/en/article/6630787>

Download Persian Version:

<https://daneshyari.com/article/6630787>

[Daneshyari.com](https://daneshyari.com)