Fuel 220 (2018) 792–799

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

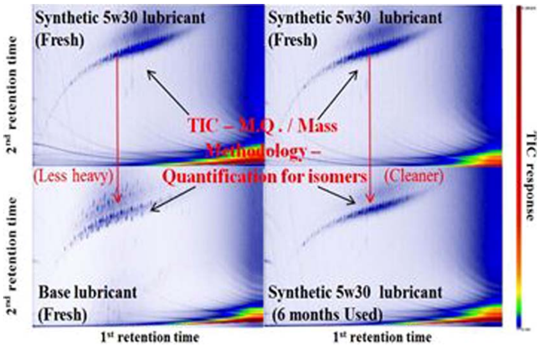
Full Length Article

Comprehensive chemical characterization of lubricating oils used in modern vehicular engines utilizing GC × GC-TOFMS

Zhirong Liang[a,b], Longfei Chen[a], Mohammed S. Alam[c], Soheil Zeraati Rezaei[b], Christopher Stark[c], Hongming Xu[b], Roy M. Harrison[c,*]

[a] *School of Energy and Power Engineering, Beihang University, Beijing 100191, China*
[b] *Department of Mechanical Engineering, School of Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*
[c] *School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom*

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Lubricants
SVOC
GC × GC-ToF-MS
Soft EI ionization
Engine oil
Hydrocarbons

ABSTRACT

A number of major studies have demonstrated that the SVOC (Semi-volatile organic compounds) within engine emissions derive predominantly from unburned fuel and lubricants, and are a major contributor to primary atmospheric aerosol containing thousands of organic compounds. The GC × GC-ToF-MS (2 dimensional Gas Chromatography – Time of Flight – Mass Spectrometry) comprehensive analytical technique was utilized in this study, to resolve the complex mixtures and characterize the SVOC content in eight different commercial lubricants, including 5 W30 synthetic and semi-synthetic, mineral and base oil. In order to quantify the aliphatic isomers, which comprise the largest component of the lubricants, a TIC-M.Q./Mass (Total ion current ratio to the molar quantity/mass) method has been developed. The TIC intensity was observed to be proportional to the molar quantity of n-alkanes for carbon number $< C_{25}$, while being linear to the mass response for these aliphatic compounds with carbon number $> C_{25}$. Additionally, the TIC intensity of the alkyl-cyclohexanes under the identical retention indices were found to have an equivalent response to those of the n-alkanes, showing that the quantitative calibrations derived for the n-alkane series could be applied to estimate the concentrations of isomeric aliphatic compounds with similar molecular weight. Furthermore, a mesh method was introduced to group the alkane species (n-alkanes, branched alkanes and cyclic alkanes etc.), combining with the use of a soft EI (electron impact) ionization (14 eV) to retain the distinct identity of the isomers with less fragmentation, which allowed the TIC-M.Q./Mass methodology to integrate all the constitutional isomers present in the lubricating oil samples. By utilizing this methodology, compositions from different samples were comprehensively compared, leading to the following conclusions: 1) the synthetic and semi-synthetic oils contained a larger

---

[*] Corresponding author also at: Department of Environmental Sciences/Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah 21589, Saudi Arabia.

E-mail address: r.m.harrison@bham.ac.uk (R.M. Harrison).

https://doi.org/10.1016/j.fuel.2017.11.142
Received 3 March 2017; Received in revised form 5 September 2017; Accepted 28 November 2017

abundance of HMW (high molecular weight) aliphatic compounds (carbon number C_{24}–C_{29}), while those in the LMW (low molecular weight range, carbon number C_{18}–C_{25}) were predominant in the mineral and base oil; 2) cycloalkanes were predominant in the synthetic and semi-synthetic oils; whereas the branched alkanes were more prominent in the mineral and base oils; 3) for lubricants used for a short period, a slight increase of LMW compounds was observed, while the HMW compounds underwent a decrease, whereas, there was an overall mass reduction for all the aliphatic compounds detected in the oil samples used for six-months.

1. Introduction

Previous studies have illustrated that vehicle emitted SVOC (semi-volatile organic compounds) are comprised of many thousands of organic compounds that are thought to be derived from unburned fuel, unburned lubricating oil, and as byproducts of incomplete combustion [1–3]. Recent studies have demonstrated a wide range (20–80%) in the contribution of unburned lubricating oil to vehicular emissions [4–6]. Worton and coworkers demonstrated that the POA (primary organic aerosol) emitted from both gasoline and diesel – powered vehicles was dominated by branched cycloalkanes, accounting for more than 80% in mass. The distribution of the aliphatic compounds in POA was inconsistent with those from the unused commercial lubricating oils, especially regarding the high molecular weight constituents [7]. Gordon et al. [8] characterized the POA emissions from several gasoline and diesel off-road engines via smog chamber experiments. They demonstrated that the POA from the 2-stroke diesel engine was 1–2 orders of magnitude higher than from light-duty gasoline vehicles because of the lubricating oil mixed with the fuel in 2-stroke engines [8]. Sonntag et al. [9] measured the PM emissions from 99 vehicles in the Kansas City Light-Duty Vehicle Emissions Study, and estimated that the contribution of lubrication oil to fleet – weighted PM was over 25% by using the survey analysis methods [9]. More recently, Yang and coworkers performed analysis of virgin lube oil, a waste lube oil and regular diesel oil and a biodiesel blend. They demonstrated that the waste lubricating oil was strongly mixed with fuel, such as diesel, biodiesel and gasoline [10]. Though many studies have demonstrated that the lubricating oils make significant contributions to the organic aerosols, little research to date has described and quantified the changes to vehicular lubricants which circulate under harsh conditions adjacent to the high temperature of the engine cylinder which can trigger decomposition and lead to an increase in the emissions, which in turn lead to organic aerosol formation [11].Comprehensive chemical analysis is necessary to fulfill the diagnostic value of source recognition and interpret the profiles in tracking oil sources, which is particularly significant for evaluation of the source apportionment of hydrocarbons in areas of heavy traffic [12]. Chemical fingerprints of lubricating oils are also key to the identification of contamination or adulteration sources [8].

Current techniques used in the analysis of oil hydrocarbons primarily include GC–MS (gas chromatography - mass spectrometry), GC-MRM-MS (GC coupled to metastable reaction monitoring and MS), GC-FID (GC coupled to flame ionization detection), HPLC (high-performance liquid chromatography), IR (infrared spectroscopy), TLC (thin layer chromatography), UV (ultraviolet), fluorescence spectroscopy and the combined usage of these techniques [13–16]. Conventional GC-FID and GC–MS have been utilized to characterize crude oils and have achieved impressive results in the past, but show many limitations due to the large contribution of the unresolved complex mixture (UCM), which is composed of many thousands of constitutional isomers of aliphatic hydrocarbons [14,17–19]. Recently, comprehensive 2D gas chromatography (GC × GC), based on the combination of two GC columns with different orthogonal stationary phases, has vastly enhanced peak resolving capacity, thus being able to identify and quantify thousands of individual compounds and classes of compounds [20] in fresh and weathered crude oils [17,20–22]. Eiserbeck and co-workers have successfully combined the techniques of GC-MRM-MS, GC × GC-FID, and GC × GC-ToFMS (Time of flight mass spectrometry) to characterize the biomarkers in tertiary oils and rock extracts, and have evaluated the differences and advantages in instrumental performance [23]. While the GC × GC-FID results displayed improved peak shape, clear quantitative peak areas and high reproducibility; GC × GC-TOFMS analysis provided higher resolution separation, retaining full mass spectra throughout the whole chromatogram. However, the significant fragmentation observed due to electron impact (EI) ionization (70 eV) yields many smaller fragments, which makes it difficult to differentiate structurally similar compounds. More recently, Worton and co-workers used GC/VUV-MS (GC coupled to vacuum ultraviolet ionization mass spectrometry), which substantially reduced fragmentation of the molecular ion and facilitated the classification of hydrocarbon compounds, hence improving isomer resolution, to analyze Gulf of Mexico crude oil. By adopting this technique, linear alkanes and branched alkanes and cycloalkanes were quantitatively distinguished with 8%, 11% and 37% respectively, indicating that cycloalkanes dominated the mass of the crude oil [3,7]. By using the HPLC system coupled to a UV detector and a high resolution quadrupole TOF-MS, Kreisberge and coworkers explored the methods capable of performed phase extraction effectively, which was successfully adopted to observe the degradation processes of the products in used engine oils [24].

In this study, GC × GC-ToF-MS combined with both hard (70 eV) and soft ionization (14 eV), was utilized for characterization of eight different motor lubricating oils. This methodology adopted lower ionization energies, leading to less fragmentation, thus retaining the molecular ion and maximizing its signal/noise ratio [25], and provided an alternative to GC/VUV-MS. A large number of isomeric organic compounds between C_{13}–C_{32}, in the previous UCM of all the motor oil samples have been separated and identified. Furthermore, a quantification methodology based on the relationship of TIC (Total ion current) to M.Q. (Molar quantity)/Mass, has been examined and successfully adopted to quantify and compare fresh and used lubricants, giving insights into the extent of compositional differences.

2. Experimental setup

2.1. Analytical instrumentation

Samples were analysed by using a gas chromatograph (GC, 7890B, Agilent Technologies, Wilmington, DE, USA) equipped with a Zoex ZX2 cryogenic modulator (Houston, TX, USA). The primary dimension was equipped with a SGE DBX5, non-polar capillary column (30 m, 0.25 mm ID, 0.25 µm – 5% phenyl polysilphenylene-siloxane). The second dimension used a polar column, SGE DBX50 (4.0 m, 0.1 mm ID, 0.1 µm – 50% phenyl polysilphenylene-siloxane), situated in a secondary oven. The GC × GC was interfaced with a BenchTOF-Select, time-of-flight mass spectrometer (ToF-MS, Markes International, Llantrisant, UK), with a scan speed of 50 Hz, covering the mass range of up to 525 m/z. Electron impact ionization energies can be tuned between 10 eV and 70 eV, the former retaining the molecular ion, while the latter causes extensive fragmentation, but allows comparison with standard library spectra [25]. Data were processed by using GC Image v2.5 (Zoex Corporation, Houston, US).