Characterization and differentiation of chemical fingerprints of virgin and used lubricating oils for identification of contamination or adulteration sources

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A B S T R A C T

Lubricating oil plays a critical role to reduce friction and to ensure the machines are more energy efficient in terms of fuel consumption and power output. The use of unqualified lube oil can result in malfunctions and damage to engines and machinery. Since petroleum-based lube oils are among the most valuable refined products, in some regions, fake, used, or waste lube oils have occasionally been deliberately adulterated into lube oil to extend the volume sold. On the other hand, used or waste lube oil is hazardous material, containing contaminants such as metals and polycyclic aromatic hydrocarbons produced by the engine during use. It becomes an environmental problem when it is purposely disposed of or accidentally spilled into the environment. Some jurisdictions now have relevant regulations to prohibit these illegal activities; therefore, forensic analysis of lube oils is essential to differentiate fake and used lube products from virgin oils, to identify and to track the adulteration source, and to identify the source of spilled oil. This work involved a fingerprinting analysis of a suite of oil samples including a virgin lube oil, used motor oils, a waste lube oil from a motor workshop, a regular diesel oil and a biodiesel blend, etc. The chemical fingerprints such as the abundance and distribution profiles of total petroleum hydrocarbon, polycyclic aromatic hydrocarbons (PAHs), particularly the higher molecular pyrogenic PAHs, and biomarkers indicate that the used and the waste lube oils are mixtures of mainly lube oil and a small amount of diesel type fuel. The presence of C_{16} to C_{20} fatty acid methyl esters (FAME) with the dominance of C16:0 and C18:1 isomers suggests that the used and the waste lube oils both contain residual palm oil-based biodiesel.

1. Introduction

Lubricating oil (or simply lube oil) is largely used in automobiles and marine engines, and other machines. Lube oil plays a critical role to reduce friction and to ensure the machines to be more energy efficient in terms of fuel efficiency and power output. Used lube oil becomes unsuitable for its original purpose due to a loss of its original properties and/or the presence of impurities. The use of substandard lube oils can result in malfunctioning and damage of engines and machinery. Since petroleum-based lubricating oils are among the most valuable products refined from crude oil, in some regions, used lube oils or other materials have occasionally been deliberately added into lube oil to extend the volume sold

[1,2]. Some jurisdictions now have relevant regulations to prevent these very profitable but illegal activities.

On the other hand, used lube oil could contain hazardous substances such as gasoline or diesel, additives, and heavy metals [3,4]. Due to potential environmental contamination and health and safety concerns, used lube oil must be recycled or disposed of properly by local waste management authorities or automotive workshops. Massive spills of lube oil rarely occur; however, frequent small chronic spillages of used or waste lube oils may pose even greater environmental problems than the accidental large spillages. In contrast to petroleum pollution, used motor oil pollution is worldwide because the major sources are automotive traffic and industrial activity. Pollution due to used motor oil reaches several million tons yearly [3,4]. Spillages of waste lube oil often involve releases from vehicles and automobile garages. Used oil can also be illegally dumped into waterways or dumped on land or in landfills to avoid payment of disposal fees, resulting

in groundwater contamination. Waste lube oil, usually as small part of the bilges from the cleaning of engine chambers of vessels, is sometimes accidentally or deliberately released into open water. The presence of lube oil in bilges serves as a valuable clue to trace the source of illegal mystery discharges [5,6].

Forensic oil analysis could be necessary to provide evidence against these illegal activities. Therefore, it is necessary to develop methodologies and protocols to characterize and distinguish the virgin, used and waste lube oils. Comprehensive fingerprinting analysis of lubricating oils is essential: (i) to better understand the physical and chemical change of used lube oil; (ii) to identify and to track the source of spilled oil; (iii) to identify the contamination source; and (iv) to differentiate fake and used lube products from virgin oils. Many spectroscopic techniques such as UV–Vis, fluorescence, infrared, and near-infrared spectroscopy have been evaluated for the application of oil analysis [7–12]. For example, Fourier transform infrared spectroscopy coupled to chemometric techniques was used to investigate high quality motor oils samples adulterated with lower quality oils, such as used oils and standard oils [2]. The spectroscopic techniques could provide convenient and rapid screening and identification of oil samples, particularly for the analysis of large number of samples during an emergency case. However, these techniques do not resolve the components in a sample; chemical information about components is embedded in multiple bands in the spectra. Spectroscopic instruments alone provide very limited information for the unambiguous identification of unknown mixtures, which is particularly true for petroleum due to its extreme complexity and variety.

Chromatographic oil fingerprinting and data interpretation techniques are widely accepted for the characterization and differentiation of petroleum oils [5,13–17]. Kaplan et al. investigated the chemical fingerprints of the "heavy ends" of crude oils including asphalts, hydraulic fluid, transmission oil, motor lubricating oils, heating oils, crude oil and coal [16]. Lu and Kaplan also studied on the difference in chemical composition for unused and used (waste) motor oils and to understand their partitioning effect in water [17]. The distribution pattern and profiles of components are, in general, different from virgin to used lube oil and from lube oil to other type of petroleum. This enables that it is possible to identify oil contamination and to track the oil source.

This approach aims to utilize the distinguishable chemical characteristics to differentiate between the used and fresh automobile lube oil (i.e., motor oil) using a gas chromatography-mass spectrometer (GC/MS). This work involved a fingerprinting analysis of a suite of oil samples including virgin lube oil, used lube oils (collected from a gasoline engine vehicle and a diesel engine vehicle), waste lube oil, regular light diesel and biodiesel blend. A multi-criterion approach was applied to identify and distinguish used and waste lube oils from the virgin lube oils. The chemical fingerprints include the abundance and distribution profiles of total petroleum hydrocarbon, polycyclic aromatic hydrocarbons (PAHs), particularly higher molecular weight pyrogenic PAHs, biomarkers and fatty acid methyl esters (FAME). The results indicate that used and waste lube oils are mixtures of mainly lube oil and a small amount of palm oil-based biodiesel.

2. Experimental

2.1. Chemicals and materials

All solvents were of the highest purity available without further purification. All glassware was cleaned to be free of target analytes prior to use.

Normal alkane and PAH calibration standard mixtures were purchased from Restek (Bellefonte, PA, USA). Deuterated internal and surrogate standards (terphenyl-d_{14}, acenaphthene-d_{10}, phenanthrene-d_{10}, benz[a]anthracene-d_{12}, and perylene-d_{12}) were purchased from Supelco (Bellefonte, PA, USA). Biomarker standards (C_{27} 5α(H),14α(H),17α(H) 20R-cholestane, C_{30} 17β(H),21α(H)-hopane C_{30} and 17β(H),21β(H)-hopane) were obtained from Chiron (Trondheim, Norway). FAME mixtures, including 37 FAME standards ranging from C_4 to C_{24} with different degrees of saturation and internal standard of heptadecanoic acid methyl ester (C17:0 ME), were purchased from Sigma–Aldrich (Bellefonte, PA, USA).

2.2. Sample preparation

The oil samples analyzed included a suite of virgin lube oil (20 W-50), a used lube oil, two waste lube oils, a diesel, and a biodiesel blend. Used lube oils #1 and #2 were collected from the motor crankcases of a gasoline-powered minivan and a diesel-powered truck in a motor workshop around Kuala Lumpur, Malaysia in September 2014. The waste lube oil was a mixture of used lube oils from a light duty diesel truck and a gasoline vehicle. The diesel and biodiesel blend are database oil provided by the Department of Chemistry, Malaysia.

An aliquot of 200 μL of oil solution (equivalent to 5–10 mg of neat oil) was spiked with appropriate surrogates and then transferred to the top of a pre-conditioned 3.0 g activated silica gel micro chromatographic column. These samples were sequentially eluted with hexane (12 mL), a mixture of hexane: dichloromethane (1:1 v/v, 15 mL), and 15 mL of dichloromethane. These fractions were carefully concentrated and spiked with appropriate internal standards (5-α-androstane for total petroleum hydrocarbon analysis, C_{30} ββ-hopane for biomarker analysis, d_{14}-p-terphenyl for PAH analysis and heptadecanoic acid methyl ester (C17:0 ME) for FAME analysis, respectively). For quality control, the ESTS reference oil (Prudhoe Bay crude oil, 13.1% weathered) was analyzed together with the oil samples.

2.3. Chromatographic sample analysis

The separation and analyses of target compounds in the oil samples were accomplished using the methods reported in our previous publications [6,18–21]. The identification and quantitation of FAMEs in the oil samples refer to our previous publications [22,23]. The GC-detectable total petroleum hydrocarbons (GC-TPH) were determined on an Agilent 6890 GC equipped with a flame-ionization detector (FID) and an Agilent 7683 autosampler. Separation and characterization of PAHs, biomarkers and FAMEs in the oil samples were simultaneously carried out on an Agilent 7890B GC interfaced to an Agilent 5977A inert mass selective detector (MSD) operated at an electron impact voltage of 70 eV in the selected ion monitoring (SIM) mode. Briefly, individual FAMEs are identified by characteristic ions from the GC–MS in the SIM modes, e.g., m/z 74 for saturated FAMEs, and m/z 55, m/z 67 and m/z 79 for monounsaturated, diunsaturated and for polysaturated FAMEs, respectively.

3. Results and discussion

3.1. Characterization of hydrocarbons in studied oil samples

Commercial lube oils consist largely of base oils and a small amount of chemical additives. Lube oil is either mineral-based or synthetic, and the mineral-based lube oils are most commonly used. To meet specific performance requirements, lube oils need to have desirable physical properties including melting and boiling points, viscosity as well as distillation range.