Characteristics of Polycyclic Aromatic Hydrocarbons Emissions of Palm-Biodiesel Blend

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Abstract. Pure diesel fuel and biodiesel/diesel blends are widely used as important materials in manufacturing and transportation industries because of increasing industrialization rate and consumption of energy worldwide. However, it causes environmental damages due to spills during their extraction, transportation, processing, and distribution. The spill simulation with pure diesel (D100) and pure palm-biodiesel (B100) and their blends (B50) have been carried out in laboratory, aiming at analyzing their polyaromatic aromatic hydrocarbons (PAHs). The procedures involved the extraction of PAHs from samples with mixtures of acetone:*n*-hexane (300, 1:1 v/v) and extracts were proceed for further cleaning with column chromatograph technique prior to GC/MS analysis. Total of 16 compounds of PAHs were determined in this study due to their toxicity potential as officially stated by United States of Environmental Protection Agency (US EPA). The results show that the blends with higher concentration of palm-biodiesel (B100) contain the lowest concentration of these compounds followed by B50 and D100. Most of quantification limits obtained for all of these compounds (between 0.06 mg/L and 11.46 mg/L) were exceeded the permitted limits of "Maximum Permissible Concentration" (MPCs) for PAHs recommended by Netherland and Canada standard quality guidelines.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds which have more than two fused aromatic rings in a linear or clustered arrangement, usually containing only carbon (C) and hydrogen atom (H) atoms, although nitrogen (N), sulfur (S) and oxygen (O) atoms may readily substitute in the benzene ring to form heterocyclic aromatic compounds. They originated mainly from human activities, including incomplete combustion of carbon-based fuels and pyrolysis of organic matter [1]. PAHs are also formed from natural sources such as forest fires and volcanic eruptions. However, most PAHs are released to the environment from anthropogenic sources such as oil spills and the burning of fossil fuels [2]. Petroleum diesel containing polycyclic aromatic hydrocarbon (PAHs) raises substantial concern because of their widely known toxic potential such as mutagenic, teratogenic, carcinogenic, photo-induced toxicity and endocrine-disrupting activities [3]. Therefore, up to sixteen compounds of PAHs are listed by the US Environmental Protection Agency (US EPA) and the European Community as priority pollutants. They are naphthalene, acenaphthene, acenaphthylene, anthracene, phenanthrene, fluorine, fluoranthene, benz[*a*]anthracene, chrysene, pyrene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[*1,2,3-cd*]pyrene. The most potent carcinogens among the PAHs are the crysene, benzo[*a*]pyrene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[*1,2,3-cd*]pyrene [4].

The aim of the study mainly focused on PAHs in the soil with biodiesel and diesel spillage simulation. The concentration of PAHs in the contaminated soil were examined and evaluated. The level of PAHs in biodiesel and diesel were compared. Our study is significant for understanding the background of PAHs level in biodiesel/diesel contaminated soil.

Materials and Methods

Material and reagents

The mixed standard solution of 16 EPA-PAHs were purchased from United State of America (USA) and further diluted to the concentration of 0.5 ppm, 1.0 ppm, 3.0 ppm and 5.0 ppm. The surrogate, 2-fluorobiphenyl (2-FBP), silica gel 60 (0.040-0.063 mm) and anhydrous sodium sulfate were also purchased from USA. All solvents (hexane and acetone) were of analytical purity and redistilled in all-glass system. The silica gel was activated in dry oven at 130 °C for 16 hours while anhydrous sodium sulfate was heated at 400 °C for 4 hours.

Experiments and sample preparation procedures

The biodiesel is palm-based biodiesel produced by transesterification with methanol was obtained from Biodiesel Pilot Plant, Faculty of Engineering Technology (FTK), University Tun Hussein Onn Malaysia (UTHM). The diesel (EN 590) was obtained from diesel pump station at Parit Raja, Johor, Malaysia. Spill simulation between pure biodiesel and diesel in soil performed according to Taylor [5], with modifications. Briefly, 500 mL of the pure biodiesel (B100) and diesel (D100) were added into plastic containers (5000 cm^3) containing 1000 g of dried soil. After that, the containers were placed in dark condition prior to further experimentations.

The soil samples were extracted according to a US EPA Method 3540C [6]. According to the method, a 10 g of dried soil samples were ground with 10 g of anhydrous sulfate. The samples were spiked with 1 mL of 2-fluorobiphenyl and extracted using mixtures of hexane/acetone via reflux circle for about 24 hours at 4-6 cycles/hour. The obtained extracts were then cleanup based on standard column chromatograph cleanup technique in a US EPA Method 3630 [7]. After that, the collect elute were concentrated using dry nitrogen gas blow down technique and submitted to GC/MS qualitative analysis aiming to identify PAHs compounds.

For GC/MS qualitative analysis, the extracts were analyzed using a gas chromatograph Agilent model TD-6890 coupled with TD-7683 autosampler, capillary column fused silica: FactorFour HP-5ms, 30 m x 0.25 mm x 0.25μm (5% phenyl, 95% methylpolisiloxane) from Agilent Inc. The instrument conditions used for analysis of extracts by GC/MS were as follows: acquisition mass range 30-450 Da, ionization mode by electronic impact (70eV). The injection volume was 1.0 μL in splitless mode, injector temperature 325 °C helium as carrier gas at 1.5 mL/min, linear velocity: 45 cm/s. Oven temp: 50 °C (hold 1 min) to 200 °C @ 25 °C/min to 326 °C @ 8 °C/min.

Results and discussion

According to the chemical analysis of the pure diesel extracts, evidenced the presence of different PAH whose main pollutant was naphthalene. The result shown the highest limit of detection for naphthalene at 11.46 mg/L, 1.05 mg/L and 0.44 mg/L in pure diesel, biodiesel/diesel blends extract respectively. This also indicated the concentration of naphthalene was higher in pure diesel extracts compared to the pure biodiesel as well as biodiesel/diesel blends extracts (Table 1).

Most of the PAH compounds, except of benzo (a) anthracene, chryrsene and benzo (k) fluoranthene in pure diesel extracts have higher concentration than biodiesel extracts. Therefore, diesel pure extracts is reconsidered to have more toxic substances than biodiesel extracts. Spillage of diesel in soils can restrain microbial activities in soils and also result in larger health impact because of their toxic potential such as cytotoxic, genotoxic, mutagenic, ferotegenic, carcinogenic, photo-induced toxicity and endocrine-disrupting activities [4].

The PAHs chemically quantified in biodiesel/diesel blends extracts refer to naphthalene (0.44 mg/L), acenaphtylene (0.38 mg/L), acenaphthene (6.40 mg/L) and phenanthrene (0.17 mg/L) a fact that can explain the direct cytotoxicity observed. The results shown that, biodiesel/diesel blends can reduce PAHs concentration and its corresponding carcogenic potency [8]. According to Schirmer [9] PAHs can cause cytotoxicity directly or after their metabolic activation via cytochrome P450. They also stated that two- and three- ring PAHs such as naphthalene, acenaphthylene, acenaphthene and phenanthrene, are recognized as direct cytoxic inducers.

Most concentration of the PAHs compounds, especially naphthalene were significantly reduced from 11.46 mg/L to 0.44 mg/L in pure diesel extracts and biodiesel/diesel blends extracts respectively. The addition of pure diesel extracts into pure biodiesel extracts with lower concentration of naphthalene at first, causing their mixtures (biodiesel/diesel blends) less concentrated.

Table 1: PAHs in soil with the mixtures of D100, B100 and B50.

Compound	Soil + D100 (mg/L)	Soil + B100 (mg/L)	Soil + B50 (mg/L)	Standard (mg/L)
Naphthalene	11.46	1.05	0.44	0.14[a]
Acenaphthylene	1.31	0.06	0.38	-
Acenaphthene	2.84	N.D	6.40	-
Fluorene	8.82	N.D	Below cal	-
Phenanthrene	5.68	0.09	0.17	0.51[a]
Anthracene	1.46	0.19	0.11	0.12[a]
Fluoranthene	0.51	N.D	N.D	2.6[a]
Pyrene	0.50	Below cal	0.03	10[b]
Benz[a] anthracene	0.30	0.47	0.26	0.25[a]
Chrysene	0.20	0.44	0.22	10.7[a]
Benzo[k] fluoranthene	0.32	0.98	0.66	2.4[a]

Indeno[1,2,3-cd] pyrene	Below cal	Below cal	Below cal	1[b]
Dibenz[a,h] anthracene	8.76	Below cal	Below cal	0.7[b]
Benzo[g,h,i] perylene	0.55	0.27	0.17	7.5[a]
TOTAL	42.71	3.55	8.84	-

Notes: a – based on Netherlands "Maximum Permissible Concentration" (MPCs) for PAHs.
b – based on Canadian Council of Ministers of the Environment environmental quality guidelines for PAHs

Conclusion

This study concluded that soil polluted with pure petroleum-based diesel (D100) has higher PAHs compounds followed by biodiesel/diesel blends (B50) and pure palm-based biodiesel (B100). The compounds of PAHs decreased with the increased amount of pure biodiesel in biodiesel/diesel blends. Although pure palm-based biodiesel (B100) is considered an eco-friendly alternative to petroleum-based diesel, the results show that some of PAHs compounds exceed the standard quality guidelines set by Netherlands and Canadian. In this study, the mixtures of pure biodiesel and diesel (referred to as B50) were capable to reduce the concentration of PAHs compounds to extent limit compared to the pure petroleum-based diesel (D100).

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