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Studies on carcinogenic PAHs emission generated by vehicles and its correlation to fuel and engine types

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The objective of this study was to find major PAHs produced in ambient air from the automobile exhaust as a function of fuels (diesel, petrol, and biodiesel) and engine type qualitatively and quantitatively. The recovery range was found between 30% and 70%. The study was carried out on two, three, and four wheelers. Biodiesel samples tested in the study were synthesized indigenously from different starting raw materials and analyzed for PAHs concentration in the exhaust on a Honda genset (EBK 2000AC Model). Biodiesel samples were blended with diesel in different ratio (25:75, 35:65 and 45:55) to investigate the exhaust behavior. Biodiesel was blended with Diesel the concentration of almost all PAHs reduces in comparison to pure Diesel exhaust. B(a)A and B(a)P was the common PAH found in higher concentration in almost all fuels. FTIR results indicate esterification of vegetable oil and NMR results indicate a complete conversion of oils into biodiesel.

Keywords: polycyclic aromatic hydrocarbons, gas chromatography, pollutants, concentration, season.

INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are quite persistent and some are known to be carcinogens[12–13]. PAHs are pollutants which are detrimental to the environment when they go beyond the threshold limit[19]. Urban PAHs concentrations have been found linked with traffic volume[15–16]. In many countries, the traffic sources have been known to be the greatest contributor of PAHs emission[1, 4–5]. A study conducted in United States of America demonstrated that motor vehicle contributes to 36% of its annual total PAH emissions of all sources[2]. In Taiwan, the effect of the traffic source on PAH emissions has been investigated by many researchers due to high traffic density within the city i.e. 475 vehicles/km^2 (highest in world). Total PAH contents at the intersection of two main roads of a city area in southern Taiwan were 5.3 and 8.3 times higher in magnitude than that in the urban and rural atmosphere[14].

The automobile industry is the second highest wealth creator in India. It is, however, a well known fact that nearly 70% of all air pollution is from vehicular emission in most of the urban environment[18]. Such kind of study could be of great significance in Indian context, especially in fast developing cities because of the varying nature of socio economical conditions of mass, road condition, traffic norms, types of vehicles that ply on the road & their age, quality of fuel and poor maintenance of road etc.

The emission factor depends on the mechanical conditions of the vehicles, load, types of fuel, types of lubricant, driving condition and presence or absence of catalytic converters etc.[20]. It is also now fairly well accepted that PAHs in the exhausts of diesel-powered vehicle include unburned fuel, lubricating oil and pyrosynthesis within the engine.

A recent report focused on the release of B(a)P from the surface coating of diesel particle soot. They reported a rapidly released pulse of B(a)P, which was quickly adsorbed through the alveolar epithelium after inhalation[7]. Atmospheric PAHs concentrations are also dependent upon the size of airborne particulate matter with the highest concentration being in the respirable size range. About 95% of total PAHs are associated with a particle size class less than 3 μm in diameter. The highest concentrations of atmospheric PAHs found in the urban environment are due to increased vehicular traffic. Shrivastava and Gajghate of NEERI Nagpur, India have studied the concentration of PAH in ng associated with per/cc of SPM (F) and PAH in ng associated with per cc of gas (A). Taking a serious note of rising air pollution levels in Delhi in 1998 Supreme Court of India directed government of Delhi to run the public modes of transport (e.g. buses, taxis and auto-rickshaws) on CNG instead of diesel fuel. The new fuel policy has led to a significant reduction in concentration levels of pollution in terms of COx, NOx, SOx and SPM in the city[17]. There is a need to study the behavior of other toxic micro pollutants in the ambient air due to a change in fuel quality standards includingthe use of biodiesel. Engines emit harmful substances depending upon the load and engine speed. A comparative evaluation of the engine exhaust emissions is only possible when specific engine testing procedures are employed. For automobiles, test cycles that contain city and highway portions should be considered.

The objective of this study was to find major PAHs produced in ambient air from the automobile exhaust as a function of fuels (diesel, petrol, and biodiesel) and engine type. The study was carried out on two, three, and four wheelers (light vehicles) on standing mode (without load conditions). Biodiesel samples were blended with diesel in different ratio (25:75, 35:65 and 45:55) to investigate the exhaust behavior.

MATERIALS AND METHODS

Materials

Commercial grade petrol and diesel samples were collected from local petrol pump. Biodiesel samples were synthesized indigenously in our laboratory from Jatropha, Linseed and Castor oils.

Reagents

Analytical grade reagents solvents and standards used in the study were procured from Merck specialty chemicals Pvt. Ltd. Mumbai, India. PAHs standards used in this study were Dr Ehrenstorfer GmbH chemicals procured through Merck, Germany. Whatman glass microfiber filter paper GF/A (20.3 x 25.4 cm) were used for the collection of air samples. The raw materials used for the synthesis of biodiesel were procured from the market.

Glasseswares

All Borosil make glassware's (A grade) were used in this study. Glassware's were dipped in nitric acid overnight and washed with the double distilled water every time before the use.

Equipments

PAHs extracted from various exhaust samples were analyzed on Nucon make microprocessor based Gas Chromatograph (GC) model No 5765 using Flame Ionization Detector. Narrow bore capillary column (BPX-5 of 60 meter length, 0.25 mm I.D. and 1 μm film thickness) used in the study was procured from SGE GmbH Germany. The injection and detector temperature were kept 280°C and 300°C respectively. Injection volume was 1 μl. The temperature was programmed for 90°C for 0.5 min, followed by 30°C/min to 290°C; hold for 5 minutes and 30°C to 320°C hold for 4 minutes. The carrier gas used was N2 (2 ml/min). Rotavapor and soxhlet extraction apparatus were used to concentrate and extract the PAHs. The exhaust samples were collected using a high volume sampler model APM-411, Envirotech Instruments Pvt. Ltd., New Delhi.

METHOD

Synthesis of Biodiesel

500 ml of vegetable oil (Castor, Linseed and Jatropha) was taken in a 1 liter round bottom flask.

The oil was heated on a hot plate cum magnetic stirrer to 60°C. 100 ml of methanol was added drop wise to the hot vegetable oil through a dropping funnel and 5 g of KOH was added to the flask with a continuous stirring till complete dissolution. The solution was stirred vigorously for another 1 hour. Heating was stopped after 1 hours and the reaction mixture was allowed to cool down for 48 hours. Two layers of liquid separate on standing; consisting of a lighter (top) biodiesel layer and darker (bottom) glycerol layer. The liquid is now transferred to a separating funnel. The glycerol and biodiesel layer was separated. Rf value of biodiesel samples was determined by using hexane and ethyl acetate (5:1) as mobile phase. The biodiesels samples synthesized were characterized for their physical properties (Table 1). Samples were also analyzed by IR and NMR to confirm the conversion.

Plan of Study

One hour sampling of engine exhaust on standing mode vehicles condition (two, three, four wheeler and Honda make genset) of different age group run on different types of fuels (petrol, diesel and biodiesel) was undertaken in the study.

Sampling method

Sampling was done from each kind of the vehicle in the standing mode run for one hour. The exhaust pipe of the vehicle was connected through a 2–2.5 inch diameter PVC pipe and left near the canopy of the high volume sampler close to the filter paper. The high volume sampler collects the particulate matters (on a glass micro fiber filter paper) in the size range varying from 100–0.01 μm along with volatile and semivolatile hydrocarbon generated by engine exhaust. The ambient air was drawn in a laminar flow at the rate of 1.01 L/min. The airborne soot particles along with PAHs were collected on filter paper (size: 8" x 10") and Polyurethane foam (PUF) plug fitted just below the filter paper in a metallic cartridge. After the sampling, filter paper along with PUF was removed and preserved in vacuum desiccators for 24 hour. The filter papers and PUF were wrapped in separate polythene bags, covered with aluminium foil and stored in refrigerator at 4°C prior to analysis. The sampling of exhaust through high volume sampler on standing vehicle is shown in Figure 1 (a) and 1 (b).

Figure 1a. Sampling of two wheeler exhaust (on standing mode) through high volume sampler

Figure 1b. Sampling of the four wheeler exhaust (on standing mode) through high volume sampler

EXTRACTION OF PAHS

PAHs (both adsorbed on particulate and vapor phase) were extracted from filter paper and PUF through soxhlet extractor using toluene as a solvent for 20 to 24 hrs at the rate of 3 cycles per hour. Toluene was used (over other solvents like benzene/methanol, dichloro methane etc.) due to its high recovery, especially for higher boiling PAHs[3] (Caricchia et al., 1999). The combined extract of filter paper and PUF was concentrated to 1ml volume in a rotary flash evaporator at 60°C under vacuum.

Table 1. Physical properties of the biodiesel samples

Physical Parameter	Types of biodiesel			Standard limits	Standard Methods
	Jatropha	Linseed	Castor		
Flash point (°C)	175.0	442.0	190.0	>101	EN ISO 3679
Pour point (°C)	13.00	10.00	23.0	> 10	ASTM D2500
Density (g/ml)	0.86	0.85	0.92	0.86–0.90	EN ISO 3675
Viscosity (Cst)	5.20	2.90	3.20	1.9–5.0	ASTM D445
Acid value (wt%)	0.33	0.22	4.00	<0.5	EN 14104
Iodine value (cg Iodine/g oil)	91.00	110.0	127.0	<120	EN 14111
Ester content (%)	99.00	100.0	96.0	>96.5%	^{1}H NMR
Esterification	yes	yes	yes	Functional group	IR

The temperature of the water bath was kept below 60°C to rule out any possibility of thermal breakdown. The extract was transferred to a 10 ml volumetric flask and the volume was adjusted to 10 ml with hexane. Impurities were removed by liquid-solid chromatography using silica gel (70–230 mesh) activated at 250°C for 24 h.

The silica gel slurry of hexane was packed in a glass micro column (15 cm long and 0.6 cm internal diameter). The concentrated extract was transferred to the top of the column and eluted with 10 ml of hexane followed by 20 ml of 1:1 solution of toluene and hexane. The eluate thus obtained was evaporated nearly to dryness using the rotavapor below 60°C. The reduced volume of the sample was dissolved in HPLC grade toluene before injecting in gas chromatograph. The sample was preserved in an amber colour sample tubes in the refrigerator below 40C till analysis. The procedure described above has been checked for recovery efficiencies using spiked PAHs standard. The recovery range between 30% and 70% with the lower value corresponds to the lower molecular weight PAHs compound. The presented data are corrected accordingly with the mean of triplicate analyses. The replicated analyses gave an error between ± 10% and ± 20%[8–11].

RESULTS AND DISCUSSION

Characterization of biodiesel samples Physical characterization

The biodiesel samples synthesized in the study were characterized for their physical properties. The results obtained have been given in Table 1.

The values given in Table 1 were compared with the values reported in the literature. All the values were approximately similar to the values accepted in EN and ASTM standards. The physical parameter of biodiesel indicated that vegetable oil (Castor, Linseed and Jatropha) was 99.999% converted into the biodiesel.

Chemical characterization of biodiesel samples by IR and NMR

FTIR of biodiesel samples and their raw material

Castor oil biodiesel

The FTIR result of Castor oil has been given in Figure 2a, whereas the FTIR result of the biodiesel sample has been given in the Figure 2b. FTIR spectrum of Castor (4.2) indicates peak at 3412 cm^{-1} due to –OH group, at 1743.9 cm^{-1} due to –C=O group and at 1166.5 cm^{-1} due to C-O group. Fig. 2b indicates a strong bond at 1741.0 cm^{-1} due to C=O group along with two medium bond at 1198.4 cm^{-1} and 1173.0 cm^{-1} due to C-O bond of ester moiety. From Figure 2b it was clear that there was presence of the OH group in the spectra of vegetable oil, whereas there was presence of ester group in Figure 2a which indicates that vegetable oil has been converted into the biodiesel sample.

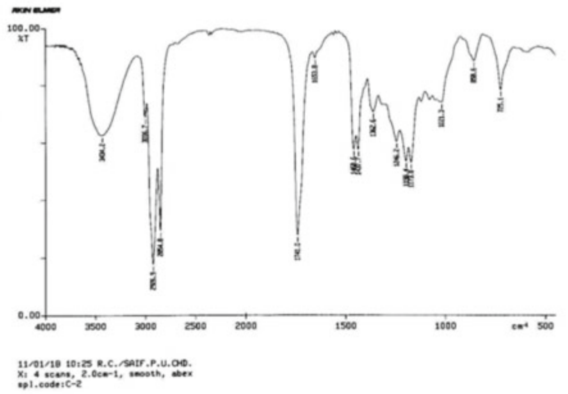

Figure 2a. IR spectra and assignment of peaks in Castor oil

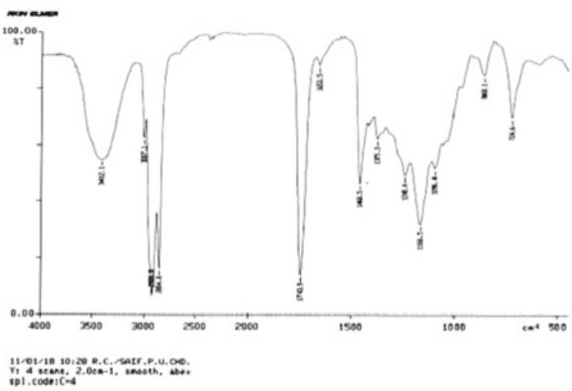

Figure 2b. IR spectra and assignment of peaks in Castor biodiesel

Linseed oil biodiesel

The FTIR result of Linseed oil has been given in Figure 2c, whereas the FTIR result of the biodiesel sample has been given in the Figure 2d. The FTIR spectrum of Linseed (4.4) indicates peak at 3466.2 cm^{-1} due to –OH group, at 1743.2 cm^{-1} due to –C=O group and at 1167.6 cm^{-1} due to C-O group. Figure 2d indicates strong bond at 1741.8 cm^{-1} due to C=O group along with two medium bond at 1197.2 cm^{-1} and 1171.7 cm^{-1} due to C-O bond of ester moiety. From Figure 2c it was clear that there was presence of OH group in the spectra of vegetable oil, whereas there was a presence of ester group in the Figure 2d which indicates that vegetable oil has been converted into the biodiesel samples.

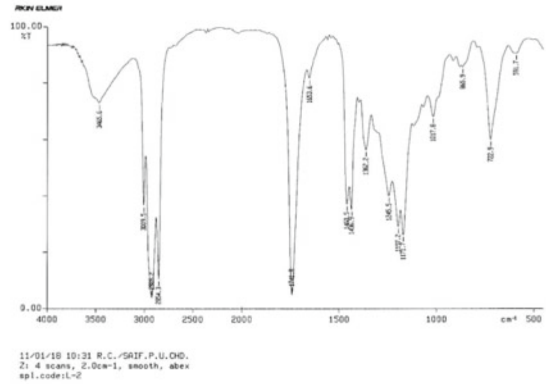

Figure 2c. IR spectra and assignment of peaks in Linseed oil

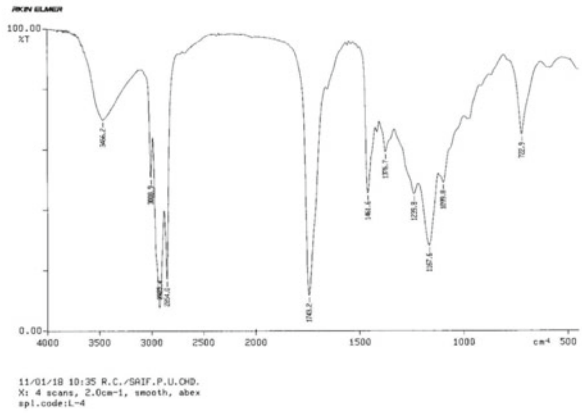

Figure 2d. IR spectra and assignment of peaks in Linseed biodiesel

Jatropha oil biodiesel

The FTIR result of Jatropha oil has been given in Figure 2e, whereas the FTIR result of the biodiesel sample has been given in the Figure 2f. The FTIR spectrum of castor (4.6) indicates peak at 3470.0 cm^{-1} due to – OH group, at 1743.9 cm^{-1} due to –C=O group and at 1167.6 cm^{-1} due to C-O group. Figure 2f indicates a strong bond at 1743.5 cm^{-1} due to C=O group along with two medium bond at 1169.9 cm^{-1} due to C- O bond of ester moiety. From Figure 2f it was clear that there was a presence of the OH group in the spectra of vegetable oil, whereas there was a presence of ester group in the Figure 2e which indicates that vegetable oil has been converted into the biodiesel samples.

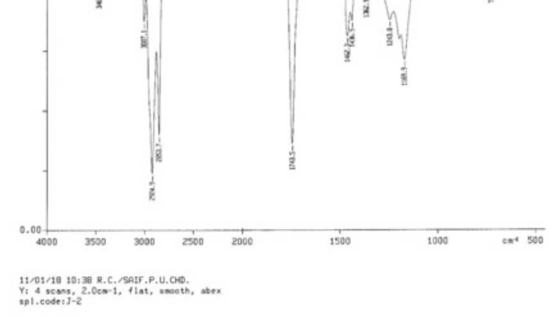

Figure 2e. IR spectra and assignment of peaks in Jatropha oil

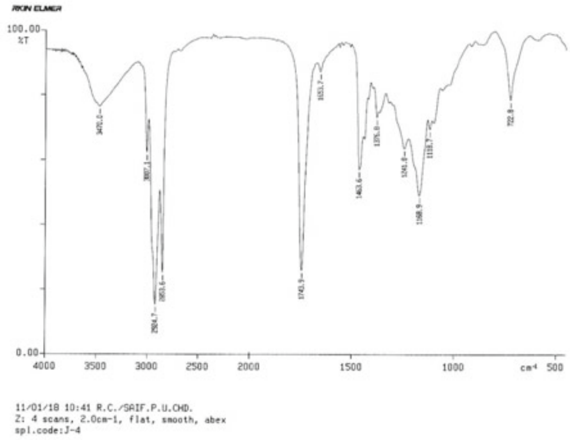

Figure 2f. IR spectra and assignment of peaks in Jatropha biodiesel

^{1}H NMR of biodiesel samples and their raw material

Formed during the transesterification reaction by following the literature reported procedure[6]. The Biodiesel so produced was further characterized and quantified by ^{1}H NMR technique (Literature reported procedure). The ^{1}H NMR spectra of vegetable oils (Fig. 3a, 3b, 3c) show a multiplet at 4.2–4.4 ppm due to the presence of glyceridic protons. The peaks in the range of 1.0–3.0 ppm in the proton NMR spectra of biodiesel and vegetable oils are due to the protons of the aliphatic hydrocarbon chain and the unsaturated protons in biodiesel as well as in vegetable oil appear at 5.4 ppm. In proton NMR

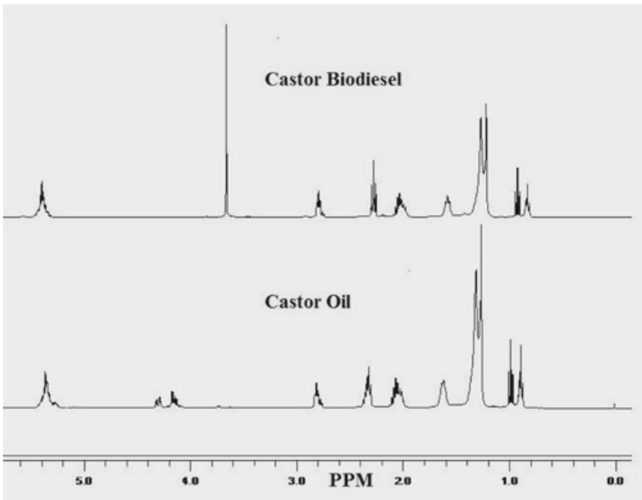

Figure 3a. ^{1}H NMR spectra and assignment of peaks in Castor biodiesel and Castor oil

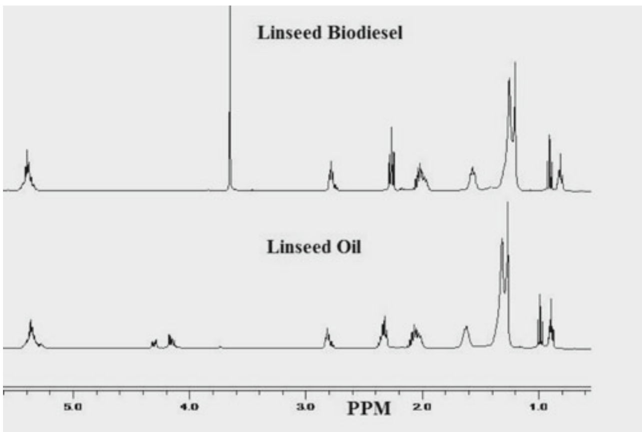

Figure 3b. ^{1}H NMR spectra and assignment of peaks in Linseed biodiesel and Linseed oil

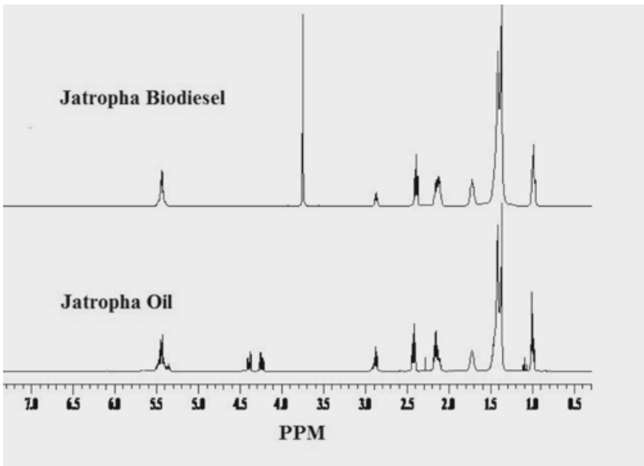

Figure 3c. ¹H NMR spectra and assignment of peaks in Jatropha biodiesel and Jatropha oil

spectra spectrum of biodiesel sample, disappearance of glyceridic protons (4.2–4.4 ppm) and appearance of a new peak at 3.6 ppm due to –O*CH3* protons support the formation of biodiesel after the transesterification reaction of vegetable oils. The Proton NMR spectra have also been used to quantify the biodiesel

% Yield = {2I(methoxy)/3I(methylene)}×100

where I(methoxy) and I(methylene) are the areas of the methoxy and methylene protons, respectively, in ^{1}H NMR spectra of biodiesel.

% Yield (Castor bio diesel) = (2 × 3.51/ 3 × 245) × 100 = 95.59= 96%

% Yield (Linseed bio diesel) = (2 ×3/ 3 × 2.03) × 100 = 98.52 = 99%

% Yield (Jatropha bio diesel) = (2 ×1.17 × 3 ×.07) 100 = 100%

The biodiesel prepared from Linseed, Castor and Jatropha biodiesel shows a complete conversion in TLC. In proton NMR analysis, the yield of prepared biodiesel samples comes out to be more than 96.5%. So, the prepared biodiesel samples found to satisfy the specification as mentioned in EN and ASTM standards. According to the EN and ASTM standard when the % yield of the biodiesel samples comes out more than 96%, it means that vegetable oil is 100% converted in to the biodiesel oil. So our NMR spectra results indicate that our vegetable oil was 100% converted in to the bio diesel samples.

Determination of PAHs in different oil samples run on different engine

In the present study, we have determined 16 EPA identified PAHs. In order to find out major contributors of PAHs in terms of concentration and types by various types of vehicles in ambient air (two, three, four wheeler and Genset) run on diesel, gasoline and biodiesel fuel; exhaust samples were collected in the standing mode from 56 exhausts.

Results of PAHs concentration for two wheelers exhausts and their correlation with engine age

Around seventeen vehicles (both scooters and bikes) with engine age ranging between 2 to 14 years were examined under this category. The results of the type and average concentration of 16 individual PAHs generated by petrol driven two wheelers have been graphically `shown in Figure 4a, whereas, Figure 4b shows average concentration of 16 PAHs (for the number of vehicles examined) versus engine age graph for the two wheelers. It could be seen from the figure that older vehicles (9–14 years) generate higher concentration (16 PAHs, 1.68–2.73 ng/m^3) of almost all PAHs as compared to the new vehicles (2–8 years, 16 PAHs, 0.48–1.76 ng/m^3) during random sampling.

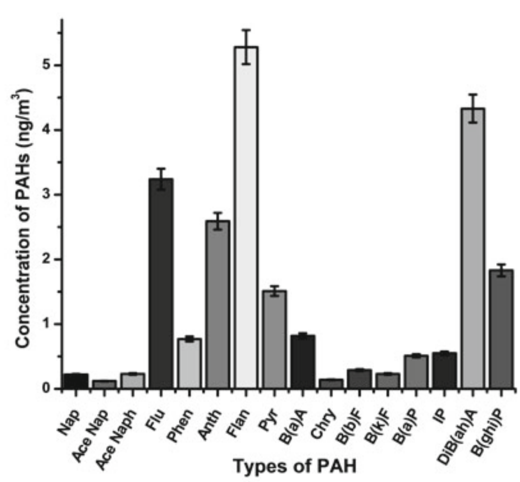

Figure 4a. Average concentration and types of 16 individual PAHs generated (petrol driven two wheelers)

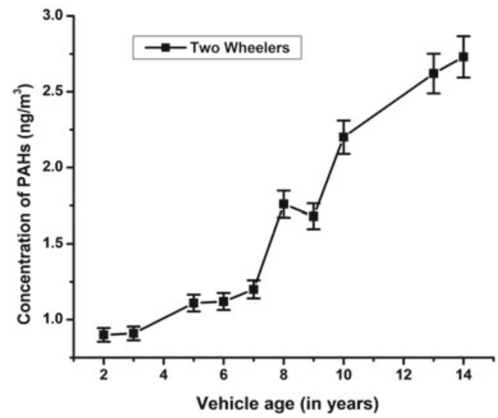

Figure 4b. Average concentration of 16 PAHs versus vehicle age graph for petrol driven two wheelers

The five major PAHs (average) found in higher concentration in the exhaust of petrol driven two wheeler were Flu (3.24 ng/m^3), Flan (5.28 ng/m^3), Dib (ah)A (4.33 ng/m^3), Anth (2.59 ng/m^3) and B(ghi)P (1.83 ng/m^3). The results shown in Figure 4a indicate that Flan & Dib(ah)A were the two individual PAH found in higher concentration i.e. 5.28–4.33 ng/m^3 (average) among all 16 PAHs. The results shown in Figure 4b indicate that there was a gradual rise in average PAHs concentration in the engine exhaust from 0.44 to 2.73 ng/m^3 with increasing age of the vehicles. It could be concluded from the Figure that concentration of PAHs is directly related to the engine age. Old vehicles (9 to 14 years) were found to generate higher concentration of PAH as compared to new vehicles (2–8 years). Hence a significant relationship between the engine age and PAHs concentration was observed for petrol driven two wheelers.

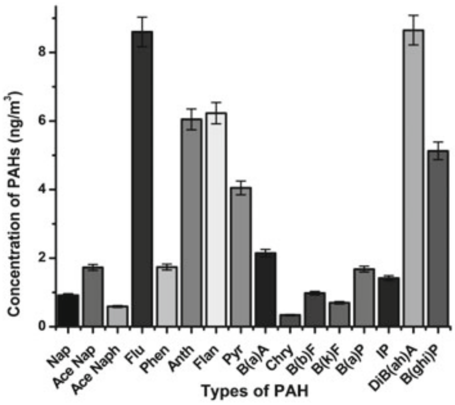

Figure 5a. Average concentration and types of 16 individual PAHs generated (Petrol driven three wheelers)

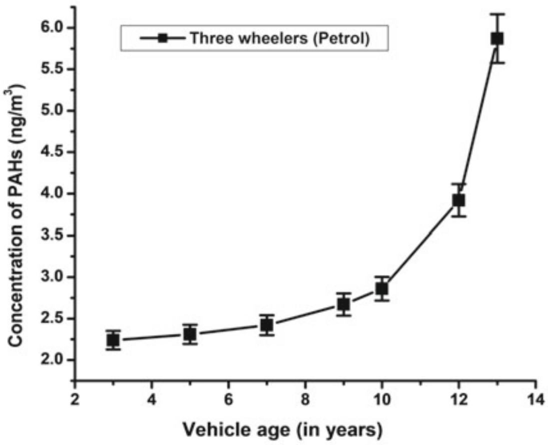

Figure 5b. Average concentration of 16 PAHs versus vehicle age graph for petrol driven three wheelers

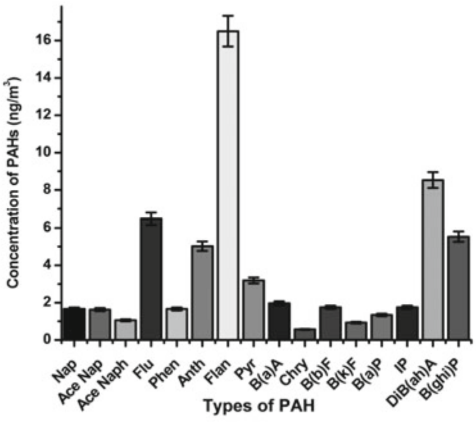

Figure 5c. Average concentration and types of 16 individual PAHs generated (diesel driven three wheelers)

Results of PAHs concentration for three wheelers (petrol and diesel) exhausts and their correlation with engine age

Around 14 vehicles (both petrol and diesel driven) with engine age ranging between 2 to 14 years were under taken in the study. The result of types and average concentration of 16 individual PAHs generated by petrol and diesel driven three wheelers has been graphically shown in Figure 5a and 5c, whereas, Figure 5b and 5d shows average concentration of 16 PAHs (for number of vehicle examined) versus engine age graph for petrol and diesel driven three wheelers respectively. It was observed that petrol driven old three vehicles (9–13

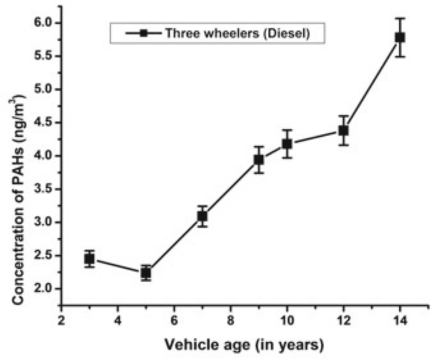

Figure 5d. Average concentration of 16 PAHs versus vehicle age graph for diesel driven three wheelers

year) generate higher concentration of 16 PAHs (16 PAHs, 2.67–5.87 ng/m^3) as compared to new vehicles (3–7 year, 16 PAHs, 2.24–2.42 ng/m^3). Flu (8.60 ng/m^3), Anth (6.05 ng/m^3), Flan (6.23 ng/m^3), Dib (ah)A (8.65 ng/m^3) and B(ghi)P (5.13 ng/m^3) were the five major PAHs found in higher concentration. Figure 5a indicate that Flu and Dib(ah)A were the two individual PAHs (average) found in higher concentration (i.e. 8.60, 8.65 ng/m^3) in petrol driven three wheeler. The result shown in Figure 5b indicates that there was a gradual rise PAHs concentration in the engine exhaust from 2.24 to 5.87 ng/m^3 with the increasing age of the vehicles.

It was concluded that PAHs concentration is directly related to the engine age. In general, a gradual rise in the concentration of all 16 PAHs in petrol driven three wheelers (individual, average and total concentration) with age was observed. Diesel driven three old wheelers (9–14 years) generate average higher concentration of 16 PAHs (16 PAHs, 3.94–5.78 ng/m^3) as compared to new vehicles (3–7 years, 16 PAHs, 2.45–3.09 ng/m^3).

Flan (16.5 ng/m^3), Flu (6.47 ng/m^3), Dib (ah)A (8.53 ng/m^3), Anth (5.04 ng/m^3) and B(ghi)P (5.53 ng/m^3) were the five major PAHs generated in higher concentration. Figure 5c also indicate that Flan and Dib(ah)A were the two individual PAHs (average) found in higher concentration (i.e. 17.47, 8.53 ng/m^3) in diesel driven three wheelers, respectively. The result shown in 5d indicates that there was a gradual rise in PAHs concentration (i.e. 2.45 to 5.78 ng/m^3) in the engine exhaust of diesel driven three wheelers. It was also observed that old (9–14 years of age) petrol and diesel driven three wheelers produce higher concentration of 16 PAHs (individual, total and average concentration) as compared to new vehicles. In general PAHs concentration was found directly related to the age of the vehicles.

Results of PAH concentration for four wheelers (light vehicle both petrol and diesel driven) exhausts and their correlation with engine age

Around 14 vehicles (light four wheelers both petrol and diesel driven) with engine age ranging between 2 to 14 years were under taken in this study. The results of types and average concentration of 16 individual PAHs generated by both petrol and diesel driven vehicles have been shown in Figure 6a and 6c, whereas, Figure 6b and 6d, indicate average concentration of 16 PAHs (for a number of vehicle examined) versus engine age graph, respectively.

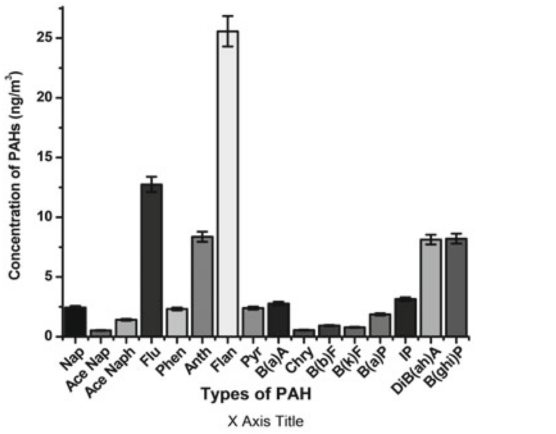

Figure 6a. Average concentration and types of 16 individual PAHs generated (petrol driven four wheelers)

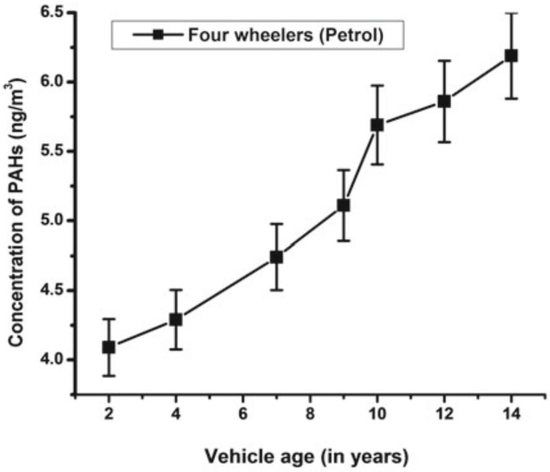

Figure 6b. Average concentration of 16 PAHs versus vehicle age graph for petrol driven four wheelers

It was observed that old petrol driven vehicles (9–14 years) generate average higher concentration of 16 PAHs (16 PAHs, 5.11–6.19 ng/m^3) as compared to new (2–7 years) vehicles (16 PAHs, 4.09–4.74 ng/m^3) during random sampling. Flan (25.57 ng/m^3), Flu (12.75 ng/m^3), Anth (8.37 ng/m^3), Dib(ah)A (8.13) and B(ghi)P (8.21 ng/m^3) were the five major PAHs produced by petrol driven four wheeler exhaust in higher concentration. Figure 6a shows that Flan and Flu were the two individual PAHs (average) found in higher concentration (12.75, 25.57 ng/m^3) in petrol driven four wheeler. The result shown in Figure 6b also indicates that there was a gradual rise PAHs concentration in the engine exhaust from 4.09 to 6.19 ng/m^3 with increasing age of the vehicles.

Figure 6c indicates that diesel driven old four wheelers (10–14 years) were found to generate higher concentration of 16 PAHs (16 PAHs, 9.23 to 11.48 ng/m^3) as compared to new (2–8 years) vehicles (16 PAHs, 6.87–8.86 ng/m^3). Flu (26.18 ng/m^3), Flan (31.66 ng/m^3), Anth (16.95 ng/m^3), DiB (ah)A (12.75 ng/m^3) and Pyr (10.62 ng/m^3) were the five major PAHs found in highest concentration in diesel driven four wheelers. Fig 6c also shows that Flu and Flan were the two individual PAHs (average) found in higher concentration (i.e. 26.18, 31.66 ng/m3) in the exhaust of diesel driven four wheelers. The result shown in Fig. 6d indicates that there was a

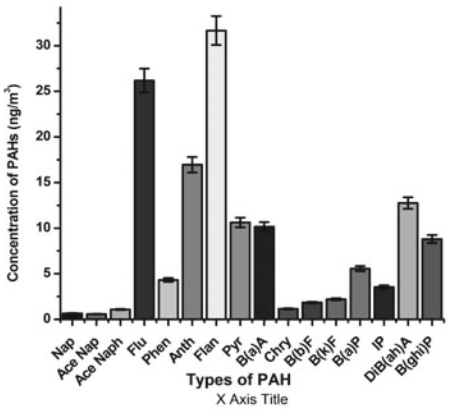

Figure 6c. Average concentration and types of 16 individual PAHs generated (diesel driven four wheelers)

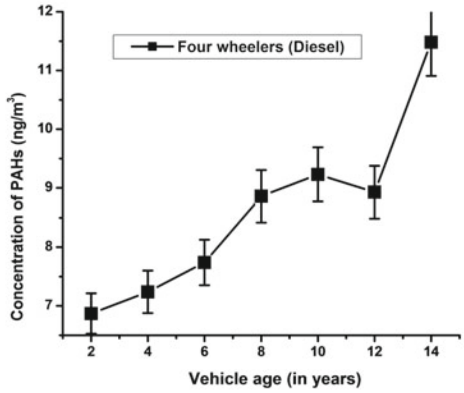

Figure 6d. Average concentration of 16 PAHs versus vehicle age graph for diesel driven four wheelers

gradual rise in PAHs concentration in the engine exhaust from 6.87 to 11.48 ng/m^3.

It was concluded that diesel driven four wheelers generate higher concentration of almost all PAHs (average, total and individual concentrations) as compared to petrol driven four wheelers. Both petrol and diesel driven old four wheelers (9–14 years of age) were found to produce a higher concentration of 16 PAHs (individual, total and average concentration). PAHs concentration was found directly related to the engine age of the vehicle.

Comparison of average concentration of 16 PAHs generated by light vehicles (two, three and four wheelers) run on various fuels in the engine exhaust

Comparison of average concentration of 16 PAHs generated by different types of vehicles examined run on different fuels has been shown in Figure 7. The figure clearly indicate that petrol driven two wheelers contribute to the lowest average PAHs concentration (between 2–14 age group), whereas, diesel driven four wheeler generate highest average concentration for the same group (2–14 years) among all types of vehicles examined. Different types of vehicles run on different fuels were found to follow following trends; Petrol (two wheelers) < petrol (three wheelers) < diesel (three wheelers) < petrol (four wheelers) < diesel (four wheelers). Flu, Flan, Anth and DiB(ah)A were the four common PAHs generated in higher concentration by almost all types of vehicles (i.e. two, three and four wheelers). Dib(ah)A are highly carcinogenic PAH identified by EPA. Whereas concentration of Dib(ah)A was highest among all kinds

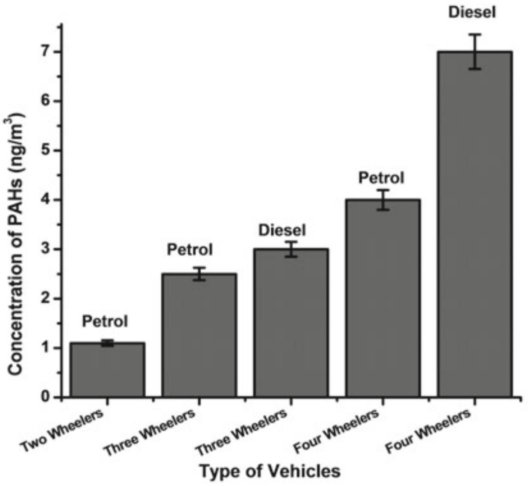

Figure 7. Comparison of average concentration of 16 PAHs produced versus type of engine

of vehicles examined, which was a dangerous sign for the peoples exposing toward these chemicals (shopkeepers, students and common man residing in the nearby areas). It can be concluded from the study that PAHs emission pattern is directly related to engine condition. Better engine condition will emit PAHs in low concentration; whereas, poor engine condition will emit PAHs in high concentration.

PAHs concentration results of Honda genset by using diesel and biodiesel fuels

In order to examine the behavior of biodiesels fuel toward PAHs generation (at different blend ratio) three biodiesel samples were synthesized indigenously from different raw materials.

The results of this study are given below:

Twelve exhaust samples of biodiesel blend with diesel run on Honda genset were undertaken in this study. The results of types and concentration of 16 PAHs generated by different biodiesel/diesel blend and fuels has been given in Table 2. The results given the Table 2 indicate that diesel generate PAHs in highest concentration (16 PAHs, 19.30 ng/m^3) and petrol generate in the lowest concentration (16 PAHs, 3.97 ng/m^3) on Honda genset. Table 2 also indicates that Linseed biodiesel/diesel blend (25:75) generate PAHs in higher concentration (16 PAHs, 19.03 ng/m^3), whereas, Linseed biodiesel/diesel blend (i.e. 45:55) generate lowest in concentration (16 PAHs, 9.04 ng/m^3) on Honda genset.

The result shown in Figure 8a, 8b and 8c indicates the type and concentration of individual PAHs generated by Jatropha, Linseed and Castor biodiesel/diesel blends (25:75, 35:65 and 45:55) run on Honda genset respectively. Figure 8a shows that in general Flu and Flan was the two individual PAHs found in higher concentration in all blends. There was a gradual reduction in the concentration of 16 individual PAHs on increasing the blend ratio from 25:75 to 45:55 (for Jatropha oil biodiesel). Figure 8b shows that in general Flan and B(a)A was the two individual PAHs found in higher concentration in all blends. There was a gradual reduction in the concentration of 16 individual PAHs on increasing the blend ratio from 25:75 to 45:55 (for Linseed oil biodiesel). Figure 8c shows that in general Flu and Flan were the two individual PAHs found in higher concentration in all blends. There was a gradual reduction in the concentration of 16 individual PAHs on increasing the blend ratio from 25:75 to 45:55 (for Castor oil biodiesel). Fig. 8a, 8b and 8c indicates that in general lower molecular weight PAHs (2, 3 and 4 ringed) were found in highest concentration as compared to high molecular weight (5 and 6 ringed) PAHs.

In biodiesel/diesel blend exhaust Linseed biodiesel produce highest PAHs concentration, whereas, Jatropha biodiesel/diesel blend produce minimum concentration. Anth (34.08 ng/m^3), Phen (12 ng/m^3), B(a)A (47 ng/m^3), Flan (122.88 ng/m^3) and Dib(ah)A (30.41 ng/m^3) were the five major PAHs generated by Linseed biodiesel/diesel blend, Nap (22.81 ng/m^3), Ace Nap (12.8 ng/m^3), Flu (130.3 ng/m^3), Anth (10.36) and Flan (29.93) were the five major PAHs generated by Jatropha biodiesel blend, whereas, Flu (80.2 ng/m^3), Anth (28.8 ng/m^3), Flan (51.1 ng/m^3), Pyr (35.4 ng/m^3) and B(a)A (15.04 ng/m^3) were five major individual PAHs generated by Castor biodiesel/diesel blend in the ratio 25:75. Anth and Flan were the two individual common PAHs found in higher

Table 2. Type and concentration of PAHs generated by biodiesel/diesel blends (25:75, 35:65 and 45:55) on Honda genset

Sr. No.	Concentration (in ng/m^3)																		
	Biodiesel/diesel	Nap	Ace Nap	Ace Naph	Flu	Phen	Anth	Flan	Pyr	B(a)A	Chry	B(b)K	B(k)F	B(a)P	IP	DiB (ah)A	B(ghi) P	Total	Average	SD
1	Jatropha 25:75	22.81	9.06	12.80	130.3	7.31	10.36	29.93	1.58	1.60	0.21	0.52	0.53	1.60	1.80	5.75	1.48	237.64	14.85	32.87
2	Jatropha 35:65	20.12	8.06	12.00	120.0	6.52	9.05	25.11	1.11	1.00	0.12	0.52	1.20	1.69	2.54	3.74	1.23	214.01	13.37	29.36
3	Jatropha 45:55	18.00	7.12	8.10	110.0	4.23	7.21	20.10	1.01	1.20	0.12	0.23	1.12	1.1	1.12	2.12	3.25	186.03	11.62	27.68
4	Linseed 25:75	0.83	1.36	2.09	8.38	12.47	34.08	122.88	3.37	47.00	1.60	1.65	5.73	10.36	11.98	30.41	10.44	304.63	19.03	30.80
5	Linseed 35:65	0.52	1.23	2.01	7.12	11.12	31.12	15.12	45.12	41.00	1.12	1.21	4.12	8.12	9.15	29.12	9.18	216.38	13.52	14.76
6	Linseed 45:55	0.12	0.12	1.11	5.12	10.12	29.12	12.12	2.12	35.00	1.01	1.02	3.12	7.12	6.15	24.12	7.15	144.64	9.04	10.89
7	Castor 25:75	0.95	0.80	3.05	80.2	14.44	28.80	51.10	35.4	15.04	2.97	1.19	4.37	7.04	5.19	11.62	7.72	269.88	16.86	22.09
8	Castor 35:55	0.29	0.60	2.58	70.12	12.02	27.12	40.18	34.12	12.14	1.12	1.14	3.12	6.11	4.12	10.14	6.12	231.04	14.44	19.32
9	Castor 45:45	0.11	0.10	1.24	50.12	10.12	25.17	30.00	31.00	11.70	1.00	1.90	1.70	5.12	3.18	6.47	4.78	183.71	11.48	14.71
10	Diesel	20.11	9.08	26.00	7.25	4.12	120.14	41.00	2.65	8.12	1.25	8.12	8.51	9.15	11.2	20.11	12.00	308.81	19.30	28.70
11	Petrol	0.12	12.10	3.10	7.12	1.12	12.30	2.03	2.14	1.12	3.12	1.12	5.02	6.01	4.01	1.02	2.10	63.55	3.97	3.74

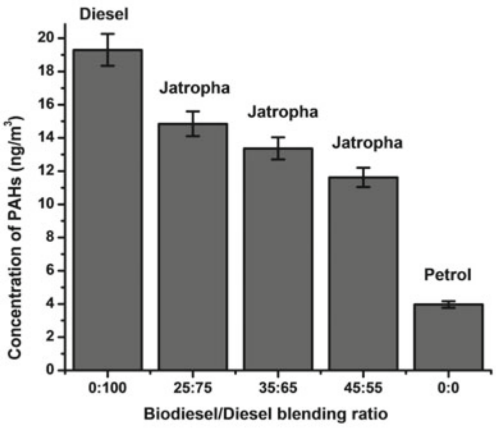

Figure 8a. Comparison of average concentration of 16 PAHs produced by pure diesel versus Jatropha oil biodiesel

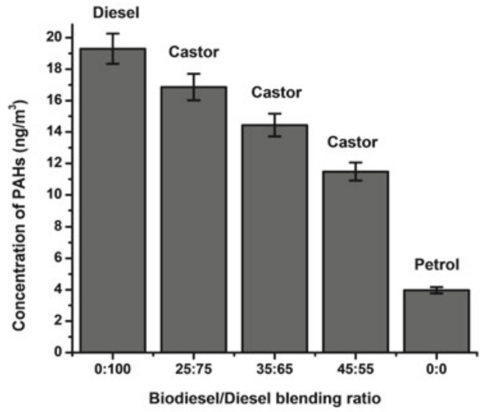

Figure 8c. Comparison of average concentration of 16 PAHs produced by pure diesel versus Castor oil biodiesel

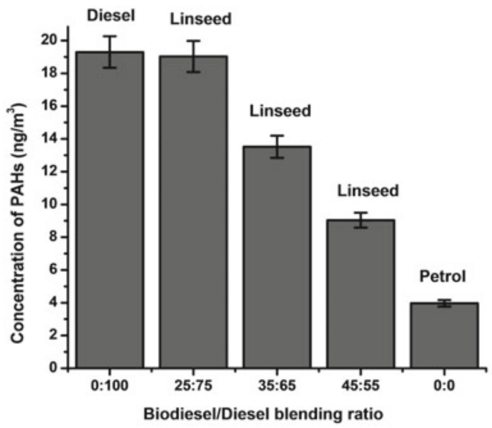

Figure 8b. Comparison of average concentration of 16 PAHs produced by pure diesel versus Linseed oil biodiesel

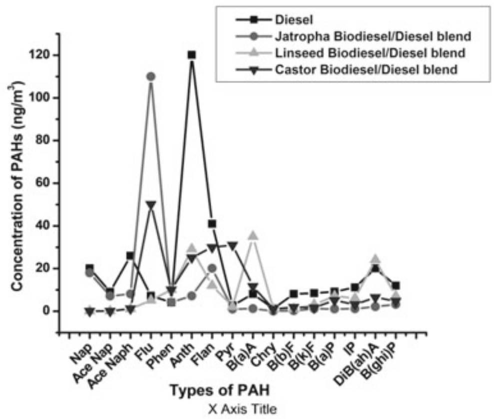

Figure 8d. Type and average concentration of PAHs generated by Jatropha, Linseed and Castor biodiesel/diesel blends on Honda genset

concentration in all five major samples (biodiesel/diesel blend 25:75).

Biodiesel was blended with diesel in different ratio i.e. 25:75, 35:65, 45:55: 55:45 given in Table 2. It was observed that blending of biodiesel with diesel was possible up to 45:55, above 45.55 it was difficult to run blending of biodiesel with diesel in genset.

Effect on blending ratio of Jatropha biodiesel with diesel on types and average concentration of PAHs: a comparative study with diesel

The result of average concentration of 16 PAHs in diesel, different Jatropha biodiesel blends and petrol on Honda genset has been graphically shown in Figure 8a. It was observed from the Figure that average concentration of 16 PAHs reduces on increasing biodiesel blend ratio from 25 to 45% as compared to pure diesel. Pure diesel generates average highest concentration of 16 PAHs i.e 19.3 ng/m^3. The average concentration was found to reduce from 19.3 to 11.62 ng/m^3 on increasing biodiesel blends ratio from 25 to 45%. PAHs emission from Honda genset was maximum for Jatropha in the ratio of 25:75 (14.85 ng/m^3) and minimum in the ratio of 45:55 (11.62 ng/m^3). In general biodiesel was found to reduce average PAHs concentration on blending with diesel from 25 to 45%.

Effect of blending ratio of Linseed biodiesel with diesel on types and average concentration of PAHs: a comparative study with diesel

The result of average concentration of 16 PAHs in diesel, different Linseed biodiesel blends and petrol on Honda genset has been graphically shown in Figure 8b. It was observed from the figure that average concentration of 16 PAHs reduces on increasing biodiesel blend ratio from 25 to 45% as compared to pure diesel. Pure diesel generates average highest concentration of 16 PAHs i.e 19.3 ng/m^3. The average concentration was found to reduce from 19.3 to 9.04 ng/m^3 on increasing biodiesel blends ratio from 25 to 45%. PAHs emission from Honda genset was maximum in the ratio of 25:75 (19.03 ng/m^3) and minimum in the ratio of 45:55 (9.04 ng/m^3). In general biodiesel was found to reduce average PAHs concentration on blending with diesel from 25 to 45.

Effect of blending ratio of Castor biodiesel with diesel on types and average concentration of PAHs: a comparative study with diesel

The result of average concentration of 16 PAHs in diesel, different Castor biodiesel blends and petrol on Honda genset has been graphically shown in Figure 8c.

It was observed from the figure that average concentration of 16 PAHs reduces on increasing the biodiesel blend ratio from 25 to 45% as compared to pure diesel. Pure diesel generates average highest concentration of 16 PAHs i.e 19.3 ng/m^3. The average concentration was found to reduce from 19.3 to 11.48 ng/m^3 on increasing biodiesel blends ratio from 25 to 45%.PAHs emission from Honda genset was maximum in the ratio of 25:75 (16.86 ng/m^3) and minimum in the ratio of 45:55 (11.48 ng/m^3). In general biodiesel was found to reduce average PAHs concentration on blending with diesel from 25 to 45%.

From the above discussion it was cleared that maximum reduction in blending of Linseed biodiesel with diesel was found to be reduced from 19.3 to 9.04 ng/m^3 (50%). Figure 8d shows a comparison of decline in individual PAHs concentration for pure diesel samples with that of biodiesel samples blends with diesel in 45:65 ratio. The graph shows that the three biodiesel diesel blends generate a lower concentration of all PAHs as compared to pure diesel samples.

In general, the results from Table 2 indicate that Nap, Flu, Ace Naph and Flan were found in higher concentration in Jatropha biodiesel blends with diesel run on Honda genset. Anth, Flan, B(a)P and Dib(ah)A was found in higher concentration in Linseed biodiesel blending with diesel run on Honda genset, whereas, Flu, Flan, Pyr and Anth was found in higher concentration in Castor biodiesel blending with diesel.

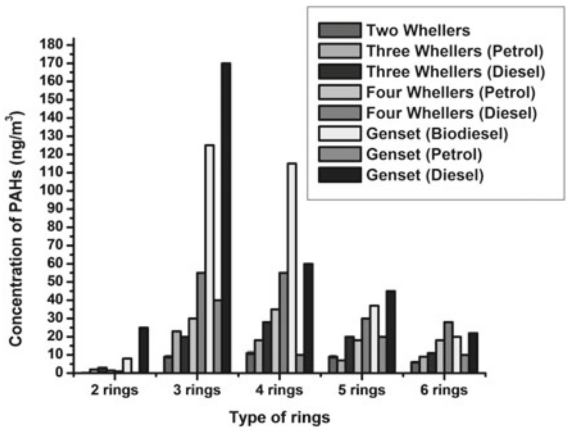

Figure 9. Ringwise distribution pattern of different PAHs collected on standing vehicles

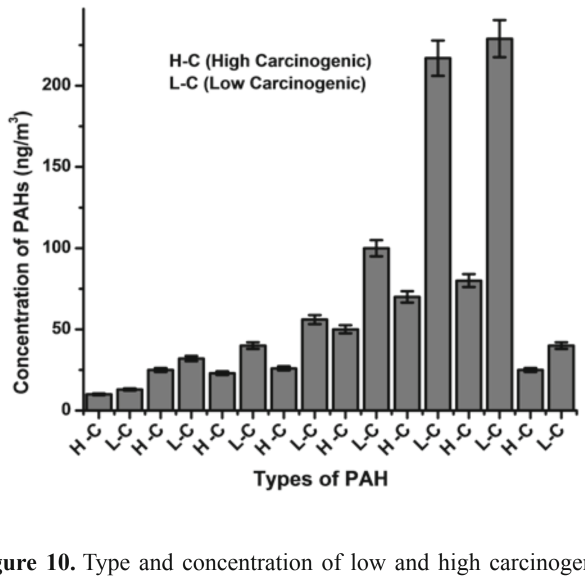

Figure 10. Type and concentration of low and high carcinogenic PAHs run on different engine

Ring wise distribution pattern of high and low carcinogenic PAHs generated by different vehicles run on different fuels

The results of ringwise distribution pattern of 2, 3, 4, 5 and 6 ringed PAHs (average percentage concentration) has been graphically shown in Figure 9. The figure indicate that four and three ringed PAHs consisting of B(a)P, B(k)F, B(b)F and Dib(ah)A were present in the highest concentration (around 70%), whereas, the two ringed PAHs were in lowest concentration (around 0.50%) in all kind of vehicle exhausts. In general the ringwise order of PAHs concentration (%) was 4> 3 >5 > 6 > 2. Among seven PAHs identified by USEPA as potential carcinogens; all the seven PAHs were observed in the current area of the study. The observed results shown B(a)A, a most carcinogenic PAHs out of 7 carcinogenic PAHs found in highest concentration in all type of rings. Figure 10 indicates that total concentration of high and low carcinogenic PAHs were not equal in all exhaust samples. The ratio of high and low carcinogenic PAHs was found to be 8.59 μg g^{-1} and 14.14 μg g^{-1} (1:1.64) for two wheelers, 20.74 and 30.28 (0.6:1) for petrol driven three wheelers, 21.83 and 37.81 (1:1.45) for diesel driven three wheeler, 25.87 and 56.40 (1:1.73) for petrol driven four wheeler & 44.87 and 93.21 (1:2) for diesel driven four wheeler respectively.

For biodiesel blend Jatropha, Linseed and Castor (45:65) the value of high and low carcinogenic PAHs were 1.68 and 22.30 (1:13), 14.43 and 13.42 (1:0.9) & 6.18 and 20.54 (1:3.32) whereas for Honda genset run on petrol and pure diesel the ratio was 20.4 and 43.14 (1.2.11) and 77.21 (1:2.99), respectively. The high ratio of high and low carcinogenic PAHs in diesel (four wheeler 1:2) and Jatropha bio diesel (1:13) engine exhaust is a sign of potential risk to the residents of the city. It can be concluded from this study that Honda Genset and diesel engine generate PAHs in higher concentration.

CONCLUSION

Petrol driven older (9–14 year) two wheeler were found to generate higher average concentration of almost all PAHs as compared to new vehicles in random sampling. The five major PAHs (average) found in petrol driven two wheeler in higher concentration were Flu, Flan, Dib(ah)A, Anth and B(ghi)P. Flan was the individual PAH found in highest concentration (5.28 ng/m^3). Diesel driven three wheelers generate higher concentration of almost all PAHs as compared to petrol driven vehicles Flan and Dib(ah)A were individual PAHs found in higher concentration in diesel and petrol driven three wheeler respectively. In general, older vehicles were found to generate higher PAHs concentration as compared to new vehicles. Diesel driven three wheelers were found to add more PAHs concentration to air as compared to petrol driven three wheelers. Flu, Flan, Anth and DiB(ah)A was the four common PAHs found in highest concentration in almost all vehicles (two, three and four wheelers). In general older vehicles were found to generate higher PAHs concentration as compared to new vehicles.

There was a gradual reduction in the concentration of 16 individual PAHs on increasing the blend ratio from 25:75 to 45:55. In general, lower molecular weight PAHs

(2, 3 and 4 ringed) were found in highest concentration as compared to high molecular weight (5 and 6 ringed) PAHs. In biodiesel/diesel blend exhaust Linseed biodiesel produce highest PAHs concentration, whereas, Jatropha biodiesel/diesel blend produce minimum concentration (25:75). Mixing of biodiesel with diesel could be a better option for PAHs reduction in diesel driven vehicles.

Biodiesel was blended with Diesel, the concentration of almost all PAHs reduces in comparison to pure Diesel exhaust. This indicates that blending of Diesel with Biodiesel reduces the concentration of almost PAHs emission and it could be a better fuel as compared to diesel in terms of carcinogenicity. Hence the chemically processed biodiesel and its blends with diesel fuel give a slightly improved performance.

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