

Development of a Formula to Quantify Emissions Generated from Diesel Vehicles in Sri Lanka

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Abstract: Unprecedented increase of greenhouse gases (GHG) have become a burning issue in the current world. Mainly Carbon dioxide (CO₂) is the most critical pollutant causing greenhouse effect. Approximately 50% of the total emissions in Sri Lanka is from transportation sector while road transportation is responsible for 88% of it. Being a CO₂ intensive country due to transportation, determination of vehicle emission levels as well as maintaining them in lower level is very important. This study is focused on the investigation of a model to calculate emission from diesel vehicle exhaust. This model was derived based on optical properties and the chemical composition of diesel exhaust. Basically CO₂, Carbon monoxide (CO), Particulate matter (PM) are the pollutants that can be quantify through the calculation procedure. Formulas derived were direct function of the K factor which is the current result of diesel vehicle emission testing program. Quantification of major pollutants of diesel exhaust is enabled from these derived formulas. Thereby decision makers could be able to verify and impose different emission standards to diesel vehicles based on the emission of pollutants rather than K factor.

Keywords: Greenhouse gases, K factor, Vehicle emissions, Carbon dioxide, Carbon monoxide, Particulate matter.

1. INTRODUCTION

Awareness of the global scale emission of greenhouse gases (carbon dioxide (CO₂), methane (CH₄), hydrofluorocarbons (CFC) and nitrous oxide (N₂O)) has increased over recent years. Researchers have found that the average CO₂ levels of Earth's atmosphere is increasing. (OECD, 2002) It was found that global CO₂ emission from transportation sector have grown by 45% during 1990 to 2007. (OECD-ITF, 2010)

In the Sri Lankan context, approximately 50% of GHG emission is via transportation sector. Even from the different transportation modes such as Sea, Air and Rail, Road transportation plays an important role being the primary mode of transportation in the country. It was observed that 88% of the total CO₂ emission from transportation sector is from road transportation while about 9% of CO₂ emission is from Air transportation. Other 3% of CO₂ emission from the transportation sector accounts the train and Sea transportation of the country. (Soezer, 2015) A significant figure of 279 Kg of CO₂ per capita has been rewarded for Sri Lanka. It describes that Sri Lanka is being most CO₂ intensive due to transportation. It is noted that an average Sri Lankan emits 300% more CO₂ from transportation, than an average person living in another region in South Asia. (South Asia region Sustainable development, 2009)

In petrol vehicles CO₂, CO and Hydro carbons (HC) are quantified under a vehicle emission test programme. But diesel vehicle emissions are not quantified. A numerical parameter named K factor (smoke density) is given which is based on the opacity of the diesel exhaust.

Smoke density is defined as a function of the number of smoke particles per unit gas volume, the size distribution of the smoke particles, light absorption and scattering properties of the particles. (Society of Automotive Engineers, 1996) Obstruction for light to travel across smoke is measured by the smoke

density which is taken as a measuring parameter for diesel emissions. In late 1800's Ringelmaan has proposed a basic method to determine Opacity of a plume. It was a visible emission evaluation system with grid system (Set of Cards) where the observer will simply compare the shade of the smoke with the shade of the card. The main drawback of Ringelmann method was that it was unable to explain the measurement exactly due to visual evaluation technique followed. So that the Opacity and the transmission of light became popular due to its accuracy and the reliability with its scientific basis. According to the Statistics of Department of motor traffic it was found that approximately 10% of the newly registered vehicles in years 2014 and 2015 are diesel fueled. Therefore, proper quantification of the 10% of annual vehicle fleet could be useful to make decisions on transportation planning.

1.1. Objective of the Study

Developing a formula to quantify CO₂, CO and PM in diesel vehicle exhaust through the K factor given at the Vehicle emission test program conducted in Sri Lanka.

2. METHODOLOGY

Using the combination of optical properties of diesel exhaust and Beer Lambert law, particulate matter concentration was derived. Major component of the particulate matter of diesel exhaust was elemental carbon which was derived from the optical properties of diesel exhaust. Characterization of diesel emission composition was done through literature. According to the Spaciate 4.0 database by United state environmental agency, characterization of diesel emission was finalized. Spaciate 4.0 shows that the diesel exhaust is a primary combination of Organic carbon (31.80%), Elemental carbon (61.20%), Sulphate (0.67%), Nitrate (0.19%) and others including metallic components and etc. (6%). Based on that, a balanced chemical equation was formed for the incomplete combustion of the diesel fuel with air. Calculation of CO₂, CO and PM was derived based on the stoichiometric ratio of the balanced chemical equation.

3. RESULTS AND DISCUSSION

Characterization of diesel was the key section of this study which was the first step of the calculation. From the information observed on Spaciate 4.0 database, combustion of diesel is further deduced in the following form.



As per the definitions and the study scope, 10 polycyclic aromatic hydrocarbons (PHA) can be identified as the organic carbons of the diesel exhaust. Namely they are;

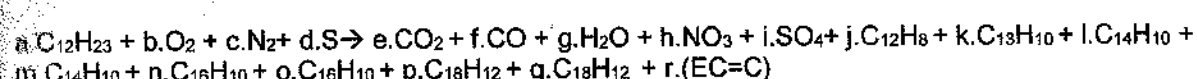
Table 1 Polycyclic aromatic hydrocarbons identified

Name of PHA	Chemical Formula	Molar Mass (g/mol)	Concentration (ng m ⁻³)	Molar Concentration (nmol m ⁻³)
Naphthalene	C ₁₀ H ₈	128	97.7	0.763
Acenaphthylene	C ₁₂ H ₈	152	83.9	0.552
Fluorene	C ₁₃ H ₁₀	166	140.2	0.844
Phenanthrene	C ₁₄ H ₁₀	178	348.0	1.955
Anthracene	C ₁₄ H ₁₀	178	31.1	0.175
Fluoranthene	C ₁₆ H ₁₀	202	37.9	0.188
Pyrene	C ₁₆ H ₁₀	202	39.8	0.197
Benzo(a)anthracene	C ₁₈ H ₁₂	228	1.4	0.006
Chrysene	C ₁₈ H ₁₂	228	3.8	0.017
Acenaphthene	C ₁₂ H ₁₀	154	61.4	0.399
Total PAH Concentration			845.2	

Identified OC's were substituted to Eq. i and the numerical coefficients of each component were taken as below.

Considering 1g of diesel exhaust,

Let a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q and r be numerical coefficients.



At engine temperature of 60°C (333K), Density of diesel exhaust = 0.98 kg/m³

According to American journal of public health and the nation's health an average fuel air ration of 0.07 will produce 1% and 13.7% of CO and CO₂. (Schrenk & Berger, 1941) Therefore,

$$CO \text{ Mass \%} = 0.01 * (1.14 / 0.98) = 11.6326 \text{ g/Kg} = 11\,632.6 \text{ } \mu\text{g/g}$$

$$CO_2 \text{ Mass \%} = 0.137 * (1.98 / 0.98) = 276.7959 \text{ g/Kg} = 276\,795.9 \text{ } \mu\text{g/g}$$

Therefore, the molecular compositions of each product from diesel combustion can be calculated as below.

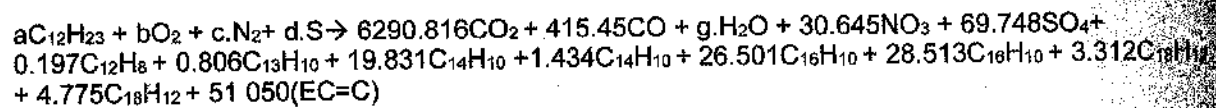
Table 2 Chemical properties of polycyclic aromatic compounds in diesel exhaust

Chemical Compound	Molar mass (g mol ⁻¹)	Composition per 1 g (µg/g)	No. of moles (µ mol)
Acenaphthylene (C ₁₂ H ₈)	152.196	30 ^b	0.197
Fluorene (C ₁₃ H ₁₀)	166.223	134 ^b	0.806
Phenanthrene (C ₁₄ H ₁₀)	178.234	3534.5 ^b	19.831
Anthracene (C ₁₄ H ₁₀)	178.234	255.5 ^b	1.434
Fluoranthene (C ₁₆ H ₁₀)	202.256	5360 ^b	26.501
Pyrene (C ₁₆ H ₁₀)	202.256	5767 ^b	28.513
Benzo(a)anthracene (C ₁₈ H ₁₂)	228.294	756 ^b	3.312
Chrysene (C ₁₈ H ₁₂)	228.294	1090 ^b	4.775
Elemental Carbon (C)	12	612 600 ^a	51050
Nitrate (NO ₃)	62	1 900 ^a	30.645
Sulphate (SO ₄)	96.06	6 700 ^a	69.748
Carbon monoxide (CO)	28	11 632.6	415.450
Carbon dioxide (CO ₂)	44	276 795.9	6 290.816

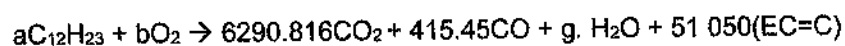
^b (Tong & Karasek, 1984)

^a (Automotive Research Association, 2009)

So the chemical equation can be simplified to;



It was clearly observed from the above table CO₂, CO, H₂O and elemental carbon are the most weighing particles in the diesel exhaust while others are less than 1% of the total mass. Therefore, the chemical equation can be further simplified as follows.



Considering C composition,

$$12a = 6290.816 + 415.45 + 51050$$

$$12a = 57756.266 \quad a = 4813.022 \mu\text{mol}$$

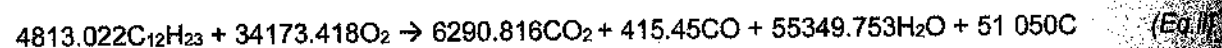
Considering H composition,

$$23a = 2g \quad g = 55349.753 \mu\text{mol}$$

Considering O composition,

$$2b = 12581.632 + 415.45 + 55349.753 \quad b = 34173.418 \mu\text{mol}$$

Therefore;



The quantification of EC of above chemical equation begins from the K factor which is the readily available information from the emission test. K factor is an optical property of particles which is also called as Opacity or extinction coefficient per volume of aerosol.

According to Beer Lambert Law;

$$I / I_0 = \exp [-bL] \quad (\text{Eq. 1})$$

I / I_0 = Refraction of transmittance
 b = Coefficient of extinction (m⁻¹)
 L = Optical path length (m)

According to Skiner and Boas-Traube;

$$I / I_0 = \exp [-S_p W L] \quad (Eq.2)$$

I / I_0 = Refraction of transmittance
 S_p = Specific extinction area (m^2/g)
 W = Total particle mass concentration
 L = Optical path length (m)

So Eq.1 = Eq.2. Therefore;

$$b = S_p W \quad (Eq.3)$$

According to Horvath and Charlson,

$$W/b = K \rho \quad (Eq.4)$$

Substituting Eq.4 to Eq.3;

$$S_p = 1 / (K \times \rho) \quad (Eq.5)$$

K = Extinction coefficient ratio
 ρ = Average particle density

Assuming the density of black aerosol is 1.95 g cm^{-3} ,

According to the work done by (Ensor & Pilat, 1971) the following information can be combined to this study.

For the Auto mobile tail pipe, geometric mean radius (r_{gw}) = 4.6 microns
 geometric standard deviation (S_g) = 31

K parameter for pollutant source automobile tail pipe is $0.059 \text{ cm}^3/m^2$,

Total particle mass concentration of black carbon was calculated as below.

From Eq.5,

$$S_p = 1 / (0.059 \times 1.95)$$

$$S_p = 8.7 \text{ m}^2/g$$

From Eq.2,

$$W = b / S_p$$

$$W = b / 8.7$$

$$W = 0.115 \times b \text{ (g/m}^3\text{)}$$

Therefore, the mass concentration of the particulate matter (BC) emitted through automobile tail pipe is $0.115 \times b \text{ (g/m}^3\text{)}$.

From the calculated BC concentration, EC can be derived as below.

$$EC = (0.115 \times b) / 0.8 = 0.144 \times b \text{ g/m}^3$$

Number of EC molar concentration;

$$EC = (0.114 \times b) / 12 = 0.0095 \times b \text{ mol /m}^3$$

Molecular ratio per 1g of exhaust air;

$$EC: CO_2 = 51 \text{ 050: } 6290.816 = 1:0.12322$$

$$EC: CO = 51 \text{ 050: } 415.45 = 1:0.008138$$

For a Volume of V, of the emission test;

$$EC = 0.0095 \times b \times V \text{ mol}$$

From the stoichiometry of balanced chemical equation,

$$\begin{aligned}\text{CO}_2 \text{ moles} &= 0.0095bV \times 0.12322 = 0.00117059bV \text{ moles} \\ \text{CO}_2 \text{ Mass} &= 51\,505.96bV \mu\text{g/g (ppm)} \quad (V \text{ in m}^{-3})\end{aligned}$$

$$\begin{aligned}\text{CO moles} &= 0.0095bV \times 0.008138 = 7.7311bV \times 10^{-6} \text{ moles} \\ \text{CO mass} &= 2\,164.708bV \mu\text{g/g (ppm)} \quad (V \text{ in m}^{-3})\end{aligned}$$

$$\begin{aligned}\text{PM moles (EC)} &= 0.0095bV \text{ moles} \\ \text{PM mass (EC)} &= 11\,400bV \mu\text{g/g (ppm)}\end{aligned}$$

Calculation of Sample volume;

$$\begin{aligned}\text{Nominal Diameter of light beam} &= 0.028125 \text{ m (Cornell University, 2016)} \\ \text{Effective optical path length} &= 0.127\text{m}^{-1} \text{ (Society of Automotive Engineers, 1996)}\end{aligned}$$

So the effective volume $(V) = 7.89 \times 10^{-6} \text{ m}^3$

Therefore;

$$\begin{aligned}\text{CO}_2 \text{ mass} &= 4.06382b \mu\text{g/g (ppm)} \\ \text{CO mass} &= 0.17079b \mu\text{g/g (ppm)} \\ \text{PM mass} &= 0.89946b \mu\text{g/g (ppm)}\end{aligned}$$

Considered densities of above components are as follows.

$$\begin{aligned}\text{CO}_2 &= 1.98 \text{ kg/m}^3 \\ \text{CO} &= 1.44 \text{ kg/m}^3 \\ \text{PM (EC)} &= 1.95 \text{ kg/m}^3 \\ \text{Diesel exhaust} &= 0.98 \text{ kg/m}^3\end{aligned}$$

Therefore, emission composition in v/v;

$$\begin{aligned}\text{CO}_2 &= 4.06382b \times (0.98/1.98) = 2.0110b \text{ (ppm v/v)} \\ \text{CO} &= 0.17079b \times (0.98/1.44) = 0.1162b \text{ (ppm v/v)} \\ \text{PM} &= 0.89946b \times (0.98/1.95) = 0.4520b \text{ (ppm v/v)}\end{aligned}$$

This calculation can be adjusted with the equipment properties. The nominal diameter of the light beam and the effective optical path length can vary with the equipment manufacturers. Only the sample volume is changed so that the coefficients of the final equation of CO₂, CO and PM will vary.

In literature it had been noticed that diesel engines are more efficient than the petrol engines thereby the CO₂, CO and HC generation is very low. The worst component found in diesel exhaust is the higher particulate matter which is an unfavourable pollutant for human beings. (Air Pollution, 2014). With these results of the work, the diesel emission standards can be revised so that the pollutants (CO₂, CO and PM) are minimized. Diesel emission standards can be controlled based on pollutant concentration as the same way conducted for petrol vehicles. Further these results can be developed to different vehicle categories available so that the emission standards can be maintained in separate standards for each vehicle category. And also these results can be used to identify the hazardous diesel vehicle types and initiate required measures to control and monitor in terms of emissions.

4. CONCLUSION

It is revealed that the diesel emission can be controlled at lower level rather than in petrol vehicles. But particulate matter emission is a disadvantage. As per the assumptions considered, when K factor is "b" diesel emissions can be determined as follows.

$$\begin{aligned}\text{CO}_2 &= 2.0110b \text{ (ppm v/v)} \\ \text{CO} &= 0.1162b \text{ (ppm v/v)} \\ \text{PM} &= 0.4520b \text{ (ppm v/v)}\end{aligned}$$

5. ACKNOWLEDGEMENTS

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