



PAH Occurrence During Combustion of Biodiesel from Various Feedstocks

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PAHs are pollutants of concern since they are known carcinogenic compounds. Their occurrence is mainly related to combustion or pyrolysis of organic matter such as fossil fuels. In the current scenario where biofuels are growingly important, it is also necessary to characterize PAH emissions due to their combustion. There are a number of works concerning PAH emissions from biodiesel combustion in Diesel engines, however, there are few regarding the difference between them depending on the feedstock and type of alcohol used in the transesterification.

The authors have processed and characterized biodiesel from several feedstocks (i.e. tallow, palm, rapeseed, soy-bean, coconut, peanut and linseed oils) to obtain FAME and FAEE and they have developed a method to measure the PAHs originated during their combustion in a bomb calorimeter. The tests have been carried out under different oxygen pressure conditions, and samples have been cleaned from the bomb after each one of these tests. The samples have been prepared for GC-MS analysis, where PAH quantities among some other combustion products have been assessed.

This work shows statistical relations obtained between the measured amounts of 18 PAHs of concern and the composition (oil and type of alcohol) used to obtain the biodiesel, and also the oxygen pressure during combustion.

1. Introduction

The European legislators may eventually require oil companies to take actions that ensure concomitant reduction in aromatic emissions. Thus, it is important to understand the mechanisms that lead to the formation of aromatic compounds during the combustion. (Rhead and Hardy, 2003) PAHs are the contaminants of most concern regarding the aromatic emissions and they are considered as the major pollutants generated from engines (Borrás et al., 2009). The burning of fossil fuels is the main source of anthropogenic PAH emission (Tavares et al., 2004) specifically exhaust emission is the most important contributor for PAH in urban areas (Ravindra et al., 2008; Karavalakis et al., 2010)

PAHs are hydrocarbons with a fused ring structure containing several benzene rings that may carry alkyl substituents. PAH occurrence in exhaust gases may be driven by: survival, the fuel PAH may survive the combustion process, retaining the original carbon skeleton, pyrosynthesis during combustion from lower molecular weight aromatic compounds, the PAH isolated in the exhaust emissions could be produced by a process whereby fragments of partially destroyed compounds could recombine to produce the new PAH, and others having the same structures as those from the fuel,

destroyed in the combustion process from various fuel sources; (Karavalakis et al., 2010b; Rhead and Hardy, 2003); pyrolysis of unburned fuel, and from unburned lubricating oil unburned and burnt fuel were shown to accumulate in motor oil, raising the amount of PAHs from undetectable in fresh oil to substantial amounts in used oil (e.g., 190 $\mu\text{g g}^{-1}$ Phenanthrene, 650 $\mu\text{g g}^{-1}$ methylphenanthrenes, and 50 $\mu\text{g g}^{-1}$ Chrysene. (Lima et al., 2005)

When the temperature exceeds 500 °C, carbon–hydrogen and carbon–carbon bond are broken to form free radicals. These radicals combine to form acetylene which further condenses with aromatic ring structures, that are resistant to thermal degradation. (Ravindra et al., 2008)

In their review (Ravindra et al., 2008) discussing about PAH source attribution, referred that three possible mechanisms suggested of PAH formation during combustion, i.e. slow Diels–Alder condensations, rapid radical reactions, and ionic reaction mechanism. However, the radical formation mechanism is favoured as the combustion process within the internal combustion engine has to occur very rapidly. It seems that gaseous hydrocarbon radicals rearrange quickly, providing the mechanism of PAHs formation and growth. The addition of hydrocarbon radicals to lower molecular weight PAHs then leads, via alkyl PAHs, to the formation of higher PAHs. Recently, (Lima et al., 2005) reviewed and discussed some of the factors (type of fuel, amount of oxygen, and temperature) that affect the production and environmental fate of combustion-derived PAHs. While PAHs are present at ambient temperature in air, both as gas and associated with particles. The lighter PAHs, such as phenanthrene, are found almost exclusively in gas phase whereas the heavier PAHs, such as Benzo[a]Pyrene, are almost totally adsorbed on to particles. (Ravindra et al., 2008).

Regarding PAH and Biodiesel combustion many works have been published (Karavalakis et al., 2010a; Correa and Arbilla, 2006; Fontaras et al., 2010; Lai et al., 2010; Lin et al., 2010; Borrás et al., 2009; Tsai et al. 2010), but few of them have studied it's relation with the biodiesel composition (Karavalakis et al. 2010a; Karavalakis et al. 2011a; Karavalakis et al., 2011b; Ballesteros 2010) and almost any correlation works suggested that PAH concentrations increased with increasing unsaturation. And none of them compared the combustion products depending on the alkyl group, for instance FAME or FAEE. Karavalakis (2010a, 2010b) sketched an alternative Diels-Alder reaction between two FAME compounds that is consistent with the analyses done in this work.

2. Experimental

2.1 Materials

Methanol and absolute ethanol were of commercial grade (Panreac) and were used without any further purification. Dichloromethane (Merck) was of HPLC grade. The catalytic solution of sodium methoxide 25 % wt. in methanol was bought from Acros Organics. Magnesium silicate Magnesol D-60 was kindly supplied by The Dallas Group of America. Silicagel (Aldrich) and was activated before use. Oxygen for the combustion pump was of 99.99 % purity.

Rapeseed, soybean and palm oils and yellow animal fat were supplied by Combustibles Ecologicos Biotel SL. Coconut (Across Organics), peanut oil (in this work was for edible use available in supermarkets) and linseed oil (Fisher Scientific) were of commercial grade.

2.2 Procedures

Degumming and esterification (if necessary) and transesterification of oils/fats have been carried out following a method previously described in the literature (Canoira et al. 2008) with minor modifications: after transesterification, alcohol (methanol or ethanol) was removed in a rotary evaporator, then it was centrifuged for 10 min at 3500 rpm, and finally traces of soap, glycerol and other pollutants were removed via dry wash with Magnesol D-60.

FAME and FAEE tests: some of the tests included in the EN14214 standard were carried out on the synthesized FAME and FAEE. Following standard procedures and the laboratory equipment used to perform the tests. The EN14214 standard refers only to FAME but has been also applied to FAEE in this work, since not FAEE standard still exists.

2.3 Combustion

The high calorific value of FAME and FAEE were measured in an automatic bomb calorimeter LECO AC300, burning 1.0 g of biofuel under different pure oxygen pressures: 689.5 kPa (100 psi), 1379.0

kPa (200 psi), 2068.4 kPa (300 psi) and 2757.9 kPa (400 psi). Once the combustion test has finished, the sample crucible and the bomb were washed separately with dichloromethane and the combined dichloromethane extracts were passed through a Pasteur pipette half filled with silicagel to eliminate soot particles.

In the test at 200, 300 and 400 psi of oxygen pressure, the test was repeated three times without changing nor cleaning the crucible and the bomb, in order to recover a higher amount of post-combustion products.

In the test at 100 psi, the test was carried out only once, the crucible and the bomb were washed separately with dichloromethane, recovering the soot particles present in both devices, and the combined dichloromethane extracts were passed through silicagel in the same way as described above.

2.4 PAH analysis

All dichloromethane extracts were concentrated to 1 mL in a rotary evaporator, and they were analyzed without any further handling. Concentrated samples were charged with an internal standard (Decafluorobiphenyl) and injected in the split mode (1 μ L, three times) via automatic Agilent PTV injector in a gas chromatograph / mass spectrometer system (GC-MS) Agilent GC 5975 - MS 7890, equipped with a capillary column HP5MS (30 m x 0.250 mm x 0.25 μ m). The analytical program was: initial temperature 60 $^{\circ}$ C, initial time 2 min, rate 5 $^{\circ}$ C/min during 10 min, final temperature 110 $^{\circ}$ C, final time 60 min. The column head pressure was 8.2317 psi (56.76 kPa) and the analysis was carried out at constant flow (1 mL/min).

Mass spectrometer ionizing chamber was set at 70 eV in the electronic impact mode (EI), and the Scan and simultaneous ion monitoring (SIM) modes were used, scanning from 70 to 500 Da. The PAH's analyzed and their characteristic ions were included in the EPA list of concern compounds.

3. Results and discussion

3.1 Combustion

The molecular formula of FAME's and FAEE's was calculated from the ester profile following a previously published method (Rodrigo, 2006), and their stoichiometric combustion equations are reported in Table 1 as well as the stoichiometric air fuel ratio necessary for their complete combustion [ref].

The cylindrical combustion pump dimensions are 102 mm height x 59 mm inner diameter, which gives an internal volume of 0.279 L. Thus, when the internal oxygen pressure was 100 psi (6.8 atm), the weight of oxygen was 2.60 g and that of air was 10.90 g, which is almost the stoichiometric air dosage (see Table 1). As a consequence, the tests at 200, 300 and 400 psi were done practically with twice, three and four times the stoichiometric amounts.

The relative fuel-air ratio Fr , defined as the ratio of the actual fuel-air ratio and the stoichiometric fuel-air ratio, has been calculated for each test and it is around 0.25 (for the 400 psi tests), 0.35 (300 psi), and 0.55 (200psi) which relate to usual partial load driving conditions in diesel engines (full load, between 0.7 and 0.8).

The 1.25 value corresponding to the 100 psi test does not relate to any actual driving condition, and thus the 100 psi test analysis will be excluded from this article. However it is relevant to point out that the 100 psi test showed the higher light PAH amounts, for instance, acenaphthene and acenaphthylene do not appear at higher pressures. The results of this test show usually the higher concentrations of heavier PAH too. Naphthalene presented the higher PAH amounts at 100 psi.

Considering together the tests at 100, 200 and 300psi, multivariate factorial and cluster (Euclidian distance and ward criterion) analysis have been done. These cluster analysis groups the PAH in lighter (till benzo[b]fluorantene) and heavier PAH, this is consistent with the different mechanisms of PAH formation. However anthracene and benzo[a]atracene are usually classified with the heavier PAH and depending on the number of groups made, pyrene may be associated to anthracene. Naphthalene can be classified in the lighter PAH group, but the higher amounts found indicate that it could be considered a group itself.

Table 1: Estimated ester molecular weight, combustion equations and Stoichiometric air fuel ratio

Samples	Mw gmol ⁻¹	Combustion equation	Stoichiometric air fuel ratio
FAME Peanut	302.8	$C_{18.78}H_{35.29}O_{2.00} + 26.60 O_2 \rightarrow 18.78 CO_2 + 17.64 H_2O$	12.55
FAME Coconut	233.8	$C_{14.40}H_{28.62}O_{2.00} + 20.56 O_2 \rightarrow 14.40 CO_2 + 14.31 H_2O$	12.16
FAME Fat	288.8	$C_{18.40}H_{35.52}O_{2.00} + 26.28 O_2 \rightarrow 18.40 CO_2 + 17.76 H_2O$	12.58
FAME Linseed	292.4	$C_{18.87}H_{33.47}O_{2.00} + 26.24 O_2 \rightarrow 18.87 CO_2 + 16.73 H_2O$	12.41
FAME Palm	284.1	$C_{18.06}H_{34.93}O_{2.00} + 25.79 O_2 \rightarrow 18.06 CO_2 + 17.47 H_2O$	12.56
FAEE Palm	298.1	$C_{19.06}H_{36.94}O_{2.00} + 27.29 O_2 \rightarrow 19.06 CO_2 + 18.47 H_2O$	12.66
FAME Rapeseed	294.3	$C_{18.89}H_{35.20}O_{2.00} + 26.69 O_2 \rightarrow 18.89 CO_2 + 17.61 H_2O$	12.54
FAEE Rapeseed	308.3	$C_{19.89}H_{37.20}O_{2.00} + 28.19 O_2 \rightarrow 19.89 CO_2 + 18.61 H_2O$	12.64
FAME Soybean	292.0	$C_{18.75}H_{34.55}O_{2.00} + 26.39 O_2 \rightarrow 18.75 CO_2 + 17.27 H_2O$	12.50
FAEE Soybean	306.1	$C_{19.75}H_{36.55}O_{2.00} + 27.89 O_2 \rightarrow 19.75 CO_2 + 18.27 H_2O$	12.60

Two different behaviors are observed when samples are grouped via factor analysis, usually FAME from coconut and peanut oil and FAEE from palm and rapeseed oil are classified together while FAME from animal fat, soybean and rapeseed oil are assembled in another group. The linseed and palm oil FAME results may be sorted in one group or the other depending on the data set chosen. This aggrupation trends reflect two main different behaviors, FAME from animal fat, soybean and rapeseed oil produced more PAH when burned with decreasing pressure (decreasing Fr), while the other samples behave in the opposite way. These two different behaviors have a strong implication while trying to represent the cause-effect relationships on a linear model.

Models have been tried for every PAH, with the variables such as, composition, Fr, iodine value, density, and average number of carbon and hydrogen atoms (deduced before in the FAME formulae presented). Fr which relates to the test pressure tends to be always the most meaningful and significant test condition as expected.

A model was picked for naphthalene, the variables were chosen via a step method for linear models using the BIC (Bayesian information criterion), and these were the composition on stearic, oleic, linoleic and linolenic FAME, Fr, iodine value and the interaction between both iodine value and Fr. All variables were highly significant and the model (23 degrees of freedom) presents a 0.91 adjusted R² and a 7.927-12 significance p-value. The model showed that the naphthalene amounts decreased with increasing concentrations of the four components implied (the more unsaturated, i.e. linolenic FAME the more depletion of PAH when compared to stearic FAME) and the iodine value and Fr and increased with the interaction between both of them. Strong correlations between low driving loads and high PAH exhaust emissions are found in literature (Karavalakis, 2010b)

As shown, the model is valid for almost every sample but for a few samples when considering the 300psi tests, FAEE from palm and rapeseed oil and FAME from coconut and peanut oil where their amounts are underestimated.

In Figure 1 naphthalene predicted concentrations are represented versus the actual concentrations. The bisector line is drawn in order to ease the interpretation of the graph.

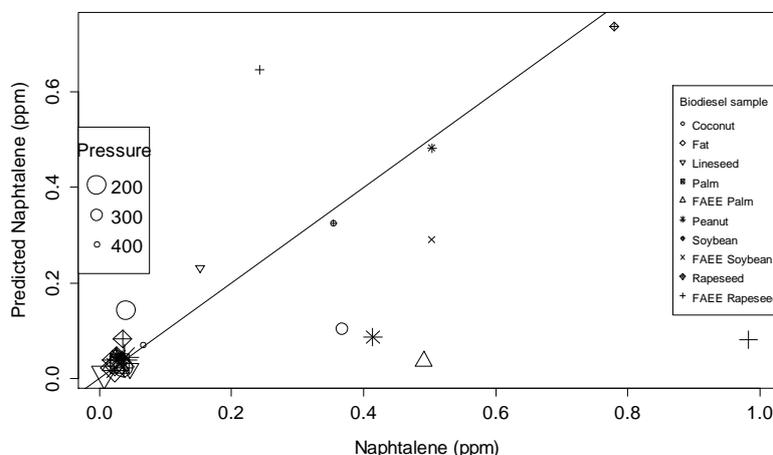


Figure 1: Predicted vs actual naphthalene concentrations

A linear discriminant analysis was made for the variables implied in the model, and grouped choosing the two different behaviors indicated before, the model variables mix rapeseed oil FAEE in the other group and does opposite for peanut FAME oil. Which might be an explanation for the bias of in the linear model for these results.

In (Karavalakis, 2010a) another Diels-Adler possible mechanism is proposed that may lead to PAH occurrence, this mechanism implies two FAME molecules that react to combine into a cyclohexene ring attached to four radicals forming a dimer FAME. This could be consistent with other products found in this work that resemble this dimer FAME.

4. Conclusion

In this work ten different biodiesels have been burned in a bomb calorimeter in order to assess the PAH amounts formed depending on their sources and type of alcohol under four different oxygen abundance conditions.

One of those conditions does not relate to an actual driving condition load in a diesel engine and therefore has been excluded from the general data treatment, however it is meaningful to point out that under those conditions the higher amounts of PAH were formed.

Except for animal fat, soybean, and rapeseed oil FAME the lower the F_r , the higher the PAH amounts. And these PAH tend to show two different behaviors when statically grouped that may relate to heavier or lighter PAH formation mechanisms.

A linear model has been carried out for naphthalene estimation where the composition in stearic, oleic, linoleic and linolenic FAME appeared as the most significant variables.

References

- Ballesteros R., Hernández J.J., Lyons L.L., 2010, An experimental study of the influence of biofuel origin on particle-associated PAH emissions, *Atmospheric Environment* 44, 930-938
- Borrás E., Tortajada-Genaro L. A., Vázquez M., Zielinska B., 2009, Polycyclic aromatic hydrocarbon exhaust emissions from different reformulated diesel fuels and engine operating conditions *Atmospheric Environment* 43, 5944–5952
- Canoira, L.; Rodríguez-Gamero, M.; Querol, E.; Alcántara, R.; Lapuerta, M.; Oliva, F. 2008, Biodiesel from Low-Grade Animal Fat: Production Process Assessment and Biodiesel Properties characterization. *Ind. Eng. Chem. Res.*, 47, 7997–8004.

- Correa S. M., Arbilla G., 2006, Aromatic hydrocarbons emissions in diesel and biodiesel exhaust Atmospheric Environment 40, 6821–6826
- Fontaras G., Karavalakis G., Kousoulidou M., Tzamkiozis T., Ntziachristos L, Bakeas E., Stournas S., Samaras Z., 2009, Effects of biodiesel on passenger car fuel consumption, regulated and non-regulated pollutant emissions over legislated and real-world driving cycles Fuel 88 1608–1617
- Karavalakis G., Deves G., Fontaras G., Stournas S., Samaras Z., Bakeas E., 2010a, The impact of soy-based biodiesel on PAH, nitro-PAH and oxy-PAH emissions from a passenger car operated over regulated and nonregulated driving cycles, Volume 89, Issue 12, December 2010, Pages 3876–3883
- Karavalakis G., Bakeas E., Fontaras G., Stournas S., 2010b, Effect of biodiesel origin on regulated and particle-bound PAH (polycyclic aromatic hydrocarbon) emissions from a Euro 4 passenger car, Energy Volume 36, 8, August 2011, Pages 5328–5337
- Karavalakis G., Bakeas E., Fontaras G., Stournas S., 2011a, An experimental study on the impact of biodiesel origin on the regulated and PAH emissions from a Euro 4 light-duty vehicle Fuel 90, 11, November 2011, Pages 3200–3208
- Karavalakis G., Boutsika V., Stournas S., Bakeas E., 2011b, Biodiesel emissions profile in modern diesel vehicles. Part 2: Effect of biodiesel origin on carbonyl, PAH, nitro-PAH and oxy-PAH emissions Science of the Total Environment, 409, 4, 738-747
- Lai J. Y.W., Lin K. C., Violi A., 2011, Biodiesel combustion: Advances in chemical kinetic modelling, Progress in Energy and Combustion Science 37, 1, 1-14
- Lima A. L. C. , Farrington, J. W. Reddy, Christopher M., 2005, Combustion-Derived Polycyclic Aromatic Hydrocarbons in the Environment-A Review, Environmental Forensics, 6: 2, 109 – 131.
- Lin Y-C., Hsu K.-H., Chen C-B., 2010, Experimental investigation of the performance and emissions of a heavy-duty diesel engine fueled with waste cooking oil biodiesel/ultra-low sulphur diesel blends Energy 36, 1, 241-248
- Rodrigo R., 2006, Producción y caracterización de biodiesel procedente de grasas animales, UCLM
- Ravindra K., Sokhi R., Van Grieken R., 2008, Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation – Review, Atmospheric Environment 42 2895–2921
- Rhead M.M., Hardy S.A., 2003, The sources of polycyclic aromatic compounds in diesel engine emissions, Fuel 82, 385–393
- Tavares M., Pinto J. P., Souza A. L., Scarmínio I. S., Solci M. C., 2004, Emission of polycyclic aromatic hydrocarbons from diesel engine in a bus station, Londrina, Brazil Atmospheric Environment 38 5039–5044
- Tsai J-H., Chen S-J., Huang K-L., Lin Y-C, Lee W-J., Lin C-C., Lin W-Y., 2010 PM, carbon, and PAH emissions from a diesel generator fuelled with soy-biodiesel blends Journal of Hazardous Materials 179, 237–243.