

# Impact of Combustion of Water in Fuel on Polycyclic Aromatic Hydrocarbon (Pah's) Precursors' Formation

Abdulaziz H. El-Sinawi

**Abstract**—Some of the polycyclic aromatic hydrocarbons (PAHs) are the strongest known carcinogens compounds; the majority of them are mostly produced by the incomplete combustion of fossil fuels; Motor vehicles are a significant source of polycyclic aromatic hydrocarbon (PAH) where diesel emission is one of the main sources of such compounds available in the ambient air. There is a big concern about the increasing concentration of PAHs in the environment. Researchers are trying to explore optimal methods to reduce those pollutants and improve the quality of air. Water blended fuel is one of the possible approaches to reduce emission of PAHs from the combustion of diesel in urban and domestic vehicles. In this work a modeling study was conducted using CHEMKIN-PRO software to simulate spray combustion at similar diesel engine conditions. Surrogate fuel of (80 % n-heptane and 20 % toluene) was used due to detailed kinetic and thermodynamic data needed for modeling is available for this kind of fuel but not available for diesel. An emulsified fuel with 3, 5, 8, 10 and 20 % water by volume is used as an engine feed for this study. The modeling results show that water has a significant effect on reducing engine soot and PAHs precursors formation up to certain extent.

**Keywords**—Polycyclic Aromatic Hydrocarbons (PAHs), Diesel Engine, Emission, Surrogate Fuel, Emulsified Fuel, Soot precursors, Combustion

## I. INTRODUCTION

DIESEL engine exhaust emissions contain hundreds of chemical compounds, which are partly emitted in the gaseous phase and partly in the particulate phase of the exhaust. The major gaseous products of combustion are carbon dioxide, carbon monoxide, nitrogen oxides, sulfur dioxide, oxygen, nitrogen, water vapor; and hydrocarbons and their derivatives. Benzene and toluene are present in the lower weight percent range in the gaseous part of the hydrocarbon fractions. Other gaseous exhaust components are low-relative-molecular-mass polycyclic aromatic hydrocarbons (PAHs). Some of the compositions of diesel exhaust gas are shown in Table 1 [1]–[3].

Diesel engine exhausts are mainly emitted from motor vehicles, stationary, railway locomotive, and ship diesel engines. The emissions from diesel motor vehicles have been well described, but the individual results are often not

comparable owing to differences in parameters such as driving cycle, engine type, and fuel composition.[2]–[4].

Increasing fuel aromaticity also increases particle emissions. PAHs and oxygenated PAHs from diesel and spark-ignition engines are qualitatively similar [4], [5]. Oxygenated and nitrated PAHs are emitted in the low microgram per kilometer range [5], [6]. PAHs emissions increase with increasing load and temperature and with the age of the engine, probably owing to increased consumption of lubricating oil [7], [8]. The aromaticity and volatility of the fuel are directly correlated with the emission of PAHs [9], [10]. Malfunction of engine devices, especially the fuel injection system, increases the emission of the main exhaust components.

## II. LITERATURE REVIEW

Very few experimental studies have been made to investigate the effect of water on the formation of polycyclic aromatic hydrocarbons. Emulsified fuels were found to give lower amounts of polycyclic aromatic hydrocarbons in the

TABLE I  
COMPOSITIONS OF LIGHT-DUTY DIESEL ENGINE EXHAUST.  
ADAPTED FROM [11, 12]

Component	Concentration (% by weight)
Carbon dioxide	7.1
Water vapor	2.6
Oxygen	15.0
Nitrogen	75.2
Carbon Monoxide	0.03
Hydrocarbons	0.0007
Nitrogen oxides	0.03
Hydrogen	0.002
Sulfur dioxide	0.01
Sulfates	0.00016
Aldehydes	0.0014
Ammonia	0.00005
Particulates	0.006

flame, as well as reduce atmospheric emissions. However unsubstantial attempts have been made to modeling these results and explain the theory behind this reduction.

Schlitt and Exner [13] have compared the output of two combustion processes in which water-in-diesel emulsion and humidified intake air techniques were used. Both techniques were effective in reducing NO<sub>x</sub> emission rate; however soot level was only reduced with emulsion.

Various water to fuel ratios were used in the combustion studies utilizing water in fuel technique. Most of the investigators focused on the effect of adding 5–10% water to fuel whereas higher ratios of water contents are rarely

Abdulaziz H. El-Sinawi; is with King Faisal University, Hofuf, Al-Hassa, 31982, Saudi Arabia, Tel. +966 (3) 580-0000 ext 5405; Cell: +966 533922745; Fax: +966 (3) 5895405, email: aelsinawi@kfu.edu.sa

discussed and needs to be thoroughly reviewed and investigated. It has been claimed that the optimum water content for  $\text{NO}_x$  and PM reduction is between 10 and 20% [14], [15].

Samec *et al.* [17] studied the effect of 10 and 20% water-in-diesel on emission reduction levels of  $\text{NO}_x$ , hydrocarbons and soot, as well as on the specific fuel consumption. The values obtained, compared to those of neat diesel show considerable reduction in both hydrocarbons and soot at 10 % water; however the 20 % water content did not significantly reduce  $\text{NO}_x$  or any of the other pollutants.

Several experimental investigations were carried out on industrial furnaces and external combustion systems [18]–[21], diesel engines [15], [16], [18], [25], [26] and gas turbines [27], [28]. All of these demonstrated the propitious aspects of using alternative and emulsified fuels; however, variations between the results from one set of experiments to another were interpreted. These variations encouraged researchers to do further investigation to clarify the results and closely understand the emulsion combustion process.

Many researchers focused on the secondary atomization and emulsified fuel penetration concepts. In the past Zhou and Thorp [30] have presented theoretical and experimental studies on the differences between pure and emulsified fuel atomization and discussed the effect of emulsified fuel atomization on fuel combustion process. They measured the spray tip penetration and spray angle of emulsion spray in a noncombusting bomb that simulated the combustion chamber of a marine diesel engine (Ruston 6APC) by using a high-speed camera with a micro-lens. Compared to the pure fuel, the emulsified fuel has longer spray tip penetration and wider spray angle. Also emulsion with water content of 5-20%, shows gradual increase in tip penetration as the water percentage increases. The number of countable droplets of emulsion fuel was much greater than that of pure fuel, and that's due to the higher total surface area of emulsion fuel droplets [31, 32, 33]. Recent studies [34] shows that the mean size of the droplets increases in accordance with the mixing ratio of the biodiesel because the viscosity and surface tension of the biodiesel are higher than those of the conventional diesel fuel. As the ratio of the biodiesel becomes higher, hydrocarbon and CO emissions are decreased, whereas the  $\text{NO}_x$  emission increases because of oxygen in the biodiesel and a shorter ignition delay, which presents a controversial mean toward investigating the hydrocarbon emission trend when water is added to fuel. Also the effect of direct water injection on decreasing flame temperature was objectively examined and investigated by Tamjima and Takasaki [35] using two simulation codes of different combustion models and by flame temperature measurement in a visual engine based on the two-colour method using special camera type, both results were in good agreement with each other and insured a significant decrease in temperature so that  $\text{NO}_x$  reduction could be clearly explained. Moreover, it was found that direct water injection could result in more complicated combustion process than

expected since preceding water vapor greatly affected the propagation and the air entrainment of the fuel spray.

Suh, Roh and Lee [36] expressed that the spray tip penetration of biodiesel fuel was similar to that of diesel. The atomization characteristics of biodiesel show that it has higher Sauter mean diameter and lower spray velocity than conventional diesel fuel due to high viscosity and surface tension. The peak combustion pressures of diesel and blending fuel increased with advanced injection timing and the combustion pressure of biodiesel fuel is higher than that of diesel fuel. It was found that the performed spray injection enhanced the combustion characteristics of biodiesel fuel caused by different physical properties of the fuel.

Sung Lin and Ping Lin [37] are recently investigate the emulsified bio diesel spray characteristics on direct injection engine emission and deposit formation. Their experimental results indicated that using emulsified biodiesel can significantly improve the fossil diesel emissions. Some potential deposit were observed, as well, during the laboratory research stage, and they succeeded in increasing the injection spray pressure by 5–10% while using 15% of water in fuel.

The approach described here aims at providing a model for emulsion spray combustion of several water-in-fuel ratios on emission criteria and mainly on the PAH formation. The modeling procedure conducted through CHEMKIN code modeling software and the fuel used is a surrogate fuel consists of 80% n-heptane and 20% toluene which represents the conventional diesel fuel.

### III. MODELING APPROACH RESULTS AND DISCUSSION

$\text{C}_3\text{H}_3$  is considered as one of the most important precursors to form PAHs molecules; hence two molecules of  $\text{C}_3\text{H}_3$  can form the first benzene ring ( $\text{C}_6\text{H}_6$ ) [38] after passing through the recombination and rearrangement as shown in the mechanism illustrated in figure 1 below. .

TABLE II  
INITIAL GAS COMPOSITION FOR CHEMKIN COMPUTATIONS

Mole Fraction[%]	$\phi$	0.8	1	2	3	5
n-heptane, $\text{C}_7\text{H}_{16}$		0.8823	1.1005	2.1685	3.202	5.191
Toluene, $\text{C}_7\text{H}_8$		0.3027	0.3795	0.7475	1.102	1.787
Oxygen, $\text{O}_2$		20.705	20.651	20.345	20.054	19.495
Nitrogen, $\text{N}_2$		78.110	77.869	76.739	75.642	73.527

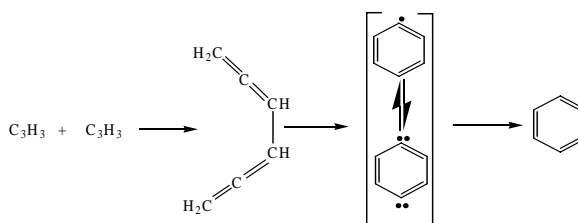


Fig. 1 Formation path of the first aromatic ring via the combination of two Propargyl ( $\text{C}_3\text{H}_3$ ) radicals, from Miller *et al.* [39]

The effect of adding water to fuel in the form of emulsion creates many different changes in the combustion process inside the PaSR reactor model which is adopted to represent the actual diesel engine for this study. Those changes affect mainly the combustion temperature and the formation of many other species such as CO, OH, NO<sub>x</sub> and soot precursors' species. The later are formed in a rich, premixed reaction zone that initiates the soot-generating reactions [40], [41]. The concentration of soot precursor species available to produce soot are strongly depending on the amount of oxygen available in the mixture. When sufficient oxygen is available, soot precursor species react with molecular oxygen or oxygen-containing radicals (OH, O, etc.) and eventually produce CO rather than aromatics and soot. Thus, this kind of reactions is considered to be another source of increasing the CO formation level. Figures 2 and 3 predict the effect of adding 3, 5, 8 and 15% water to fuel on the formation of soot precursor C<sub>3</sub>H<sub>3</sub> at two different air/fuel equivalent ratios ( $\phi=0.8, 2$ ). As shown in Figure 2, the formation of C<sub>3</sub>H<sub>3</sub> at  $\phi=0.8$  decreases when 3 and 5% water added to fuel, however, when adding more water (8 and 15 % water) to fuel, the formation of propargyl species noticeably increased. That means the formation level of soot precursors inside the PaSR reactor are very sensitive to water content. Temperature reduction and the slightly reduction in the formation of OH radicals cause the increase in soot precursors when more water is added to fuel.

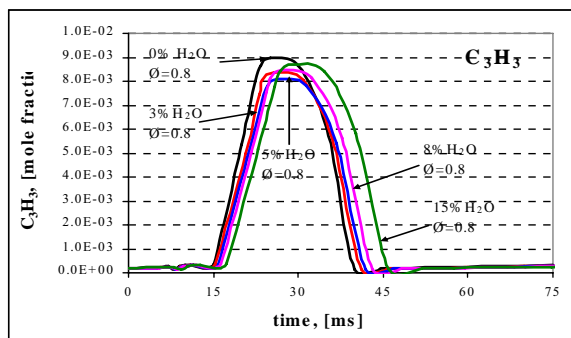


Fig. 2 Concentration of C<sub>3</sub>H<sub>3</sub> precursors change with time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, at  $\phi=0.8$

For the case of fuel-rich ( $\phi=2$ ), Figure 3 shows the change of C<sub>3</sub>H<sub>3</sub> with water content in fuel. It is clear that C<sub>3</sub>H<sub>3</sub> formation increases with the increasing amount of water in fuel, because in addition to a significant amount of fuel always remains un-oxidized at higher fuel/air equivalence ratio, soot precursors among which C<sub>3</sub>H<sub>3</sub> has a higher concentration at ( $\phi=2$ ) than that of the fuel-lean case ( $\phi=0.8$ ), as shown in Figure 3. The trend of C<sub>3</sub>H<sub>3</sub> formation illustrated in this figure predicts the affect of fuel-rich combustion at lower temperature on generating a suitable environment for soot precursors' formation.

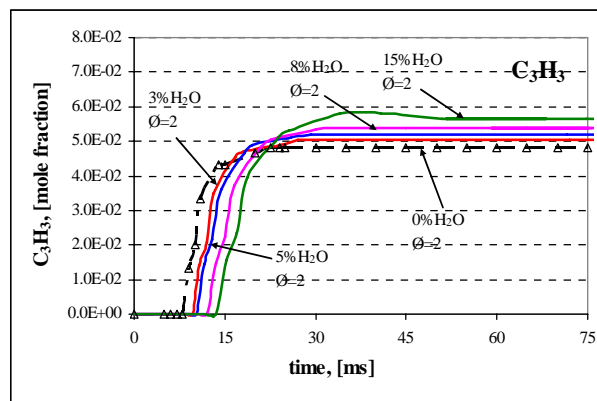


Fig. 3 Concentration of C<sub>3</sub>H<sub>3</sub> precursors change with time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, at  $\phi=2$

Diesel fuel contains a variety of different hydrocarbons, among which aromatics are the major source of smoke emissions, hence aromatics are significant contributors to the formation of soot particles in the combustion process where the chemical kinetic mechanism predicts too slow formation of PAH at low temperature. The growth of larger aromatic species follows essentially the HACA (H-Abstraction-C<sub>2</sub>H<sub>2</sub>-Addition) mechanism [43]. The HACA mechanism assumes a sequential two step process toward the formation of aromatic ring: H-abstraction, which activates the aromatic molecules, followed by acetylene addition and molecular growth then cyclization of PAH [42]–[44].

Therefore starting with a surrogate fuel (80% n-heptane and 20% toluene), which contains aromatics, predicts the importance of the “direct molecular combination” and the intact of aromatic rings. For example, in the case of high temperature pyrolysis of benzene the reactions shown in figure 4 predicts the significance of the PAH molecular growth in the initial stages [38], [42]–[44]. However, as the reaction proceeds, the initial benzene molecule decomposes to form acetylene; which increases the concentration of acetylene to be comparable with that of benzene therefore the PAH growth mechanism switches back to the HACA mechanism.

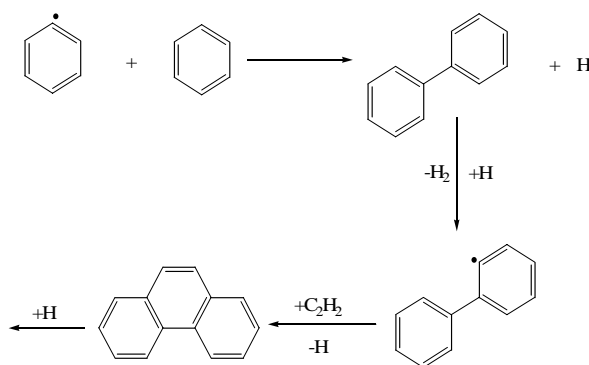


Fig.4 PAH growth initiated by aromatic combination of two benzene rings [38]

To understand the effect of adding water to surrogate fuel in the PaSR combustion model, figures 6 through 9 are plotted for several PAH compounds at 3, 5, 8 and 15 % water in fuel. It is depicted from those figures that the formation of benzene, naphthalene, phenanthrene and chrysene have the tendency to decrease at fuel lean condition when water is added to fuel. However, it decreases slowly with the increasing amount of water in fuel; therefore the 15 % water in fuel predicts the highest PAH precursor's concentrations among the other percentages of water in fuel but still lower than the concentration of the pure fuel; whereas the lowest concentration is found for 5 % water in fuel.

The formed benzene rings can combine with the available aromatic toluene compounds and play an important role in PAHs and soot formation, as illustrated in figures 1 and 4. Water play a significant role in oxidizing soot precursors either by the reactions of propargyl precursors with OH radicals before they can form the benzene rings, as shown in reaction (1), or the oxidation of the PAH precursors formed from toluene with OH radicals as shown in figure 5 .

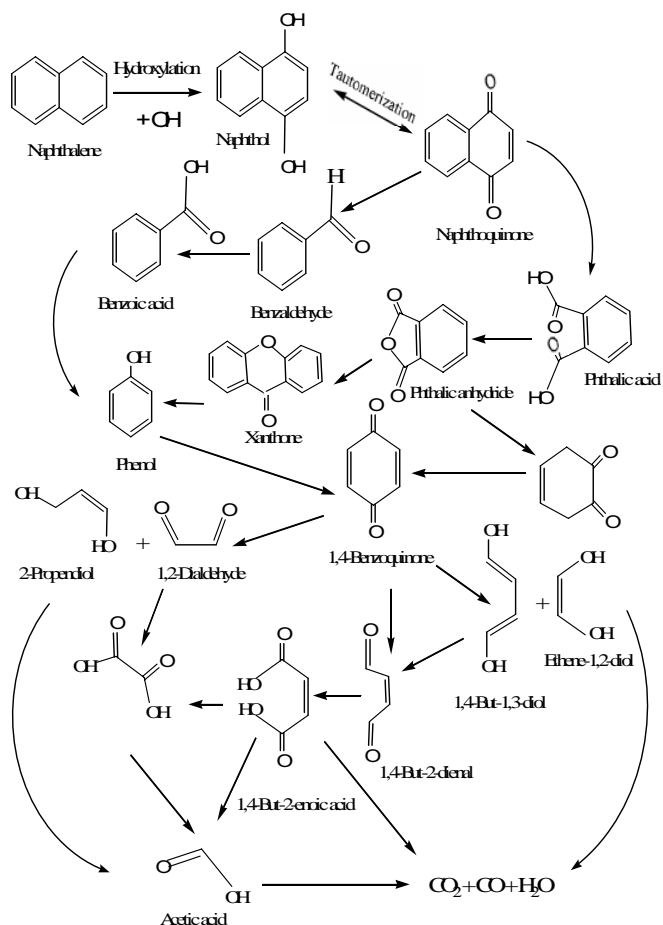


Fig. 5 Reaction mechanisms for the oxidation of naphthalene with OH radicals from Onwudili *et.al* [43]

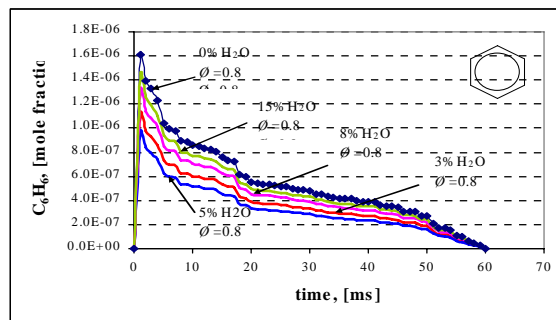


Fig. 6 Benzene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

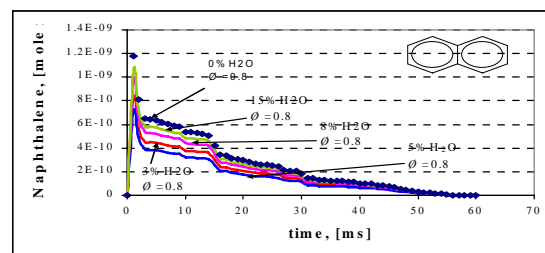


Fig. 7 Naphthalene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

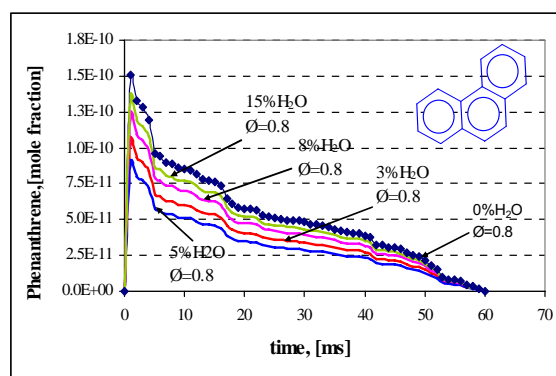


Fig. 8 Phenanthrene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

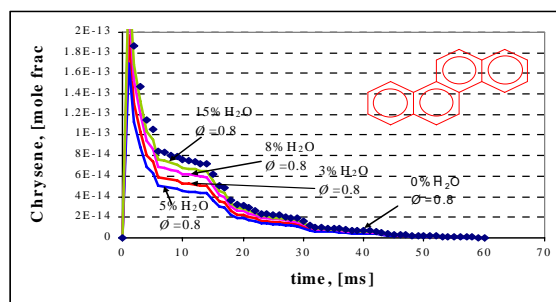


Fig. 9 Chrysene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

For higher equivalent ratio (i.e. fuel-rich), the peak PaSR model temperature decreases, whereas soot precursors formation and un-burned fuel increase as shown in figures (10-13). This would emphasize the tendency of the aromatic compounds to form soot particles at low temperature and fuel rich combustion.

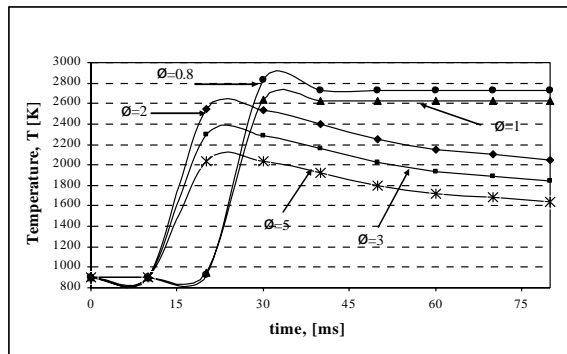


Fig. 10 Calculated temperature for air/ (80% n-Heptane+20% Toluene) mixtures of different fuel/air-equivalence ratios [45]

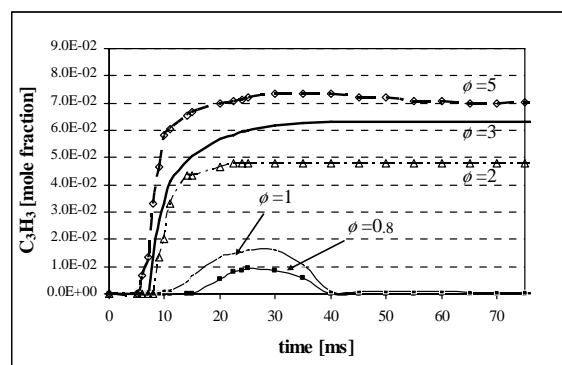


Fig. 11 Formation of soot precursor  $C_3H_3$  from the combustion of surrogate fuel (80% n-heptane and 20% toluene) at different equivalence ratios

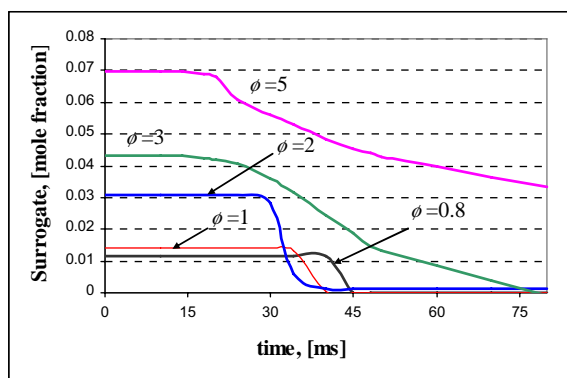


Fig. 12 Mole fraction of surrogate fuel (80% n-heptane and 20% toluene)

Adding water to surrogate fuel at fuel rich condition results in further decrease in temperature [45]. The model shows a decrease in soot precursors' formation as shown in figures 13 through 16. This reduction is significant at 5% water in fuel

which shows the lowest value, however it starts to increase slowly with the increasing amount of water in fuel up to 8% water, after that the formation tendency starts to increase and reaches the maximum at 15% water in fuel. Thus it is clear that; at fuel rich condition more water in fuel (i.e. 15% and above) may inversely affect the production rate of soot precursors.

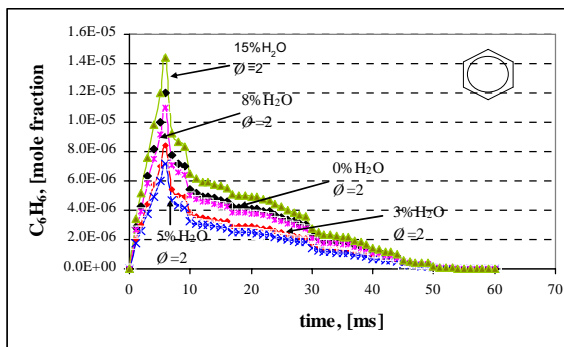


Fig. 13 Benzene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

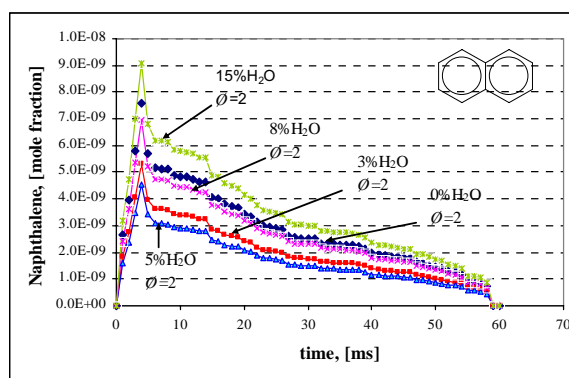


Fig. 14 Naphthalene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

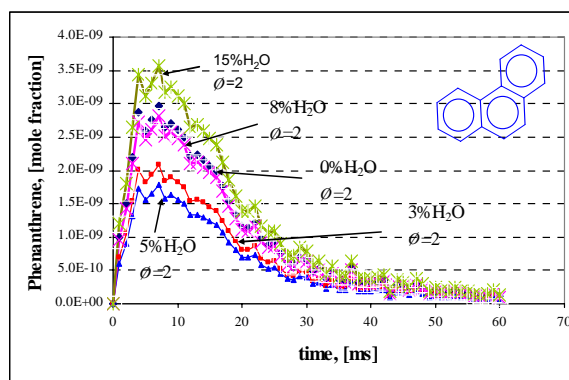


Fig. 15 Phenanthrene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

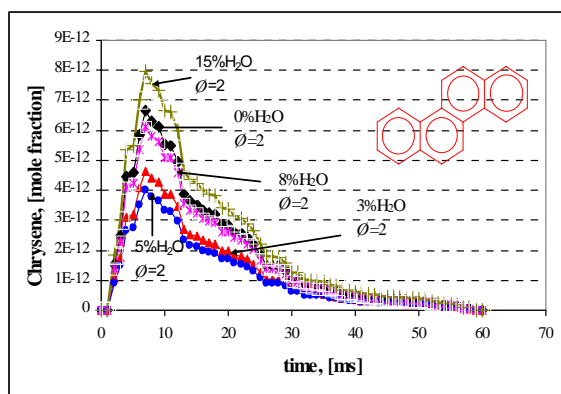


Fig. 16 Chrysene concentration change with different time at the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel

### III. CONCLUSION

A remarkable decrease in the peak value of soot precursors' formation was found after the addition of 5% water to fuel; however, this value decreased slightly with the increasing amount of water through the ratio 5 to 15%. That means extra amount of water in fuel can inversely affect soot formation level. Also It was depicted that the increase in water content of the emulsified fuel results in the increase of time lag from the start of fuel injection to the time where the peak amount of soot starts to appear. It is conceivable from the results of previous researches that the reduction in soot formation is due to a proper mixing of fuel and air which arise from secondary atomization phenomena and the decrease of flame temperature. However in this work; two possible effects have been hypothesized by which addition of water vapor can affect soot formation: a thermal effect and a chemical effect. The thermal effect is due to the reduction in the flame temperature which results in reducing the formations level of soot precursors and the chemical effect was attributed to changes in the radical pool by the presence of water vapor which enhances the formation of hydroxyl radicals to subsequently attack the soot precursors and suppress their formation.

The effect of equivalent ratio in this analysis is very clear: It is depicted that at fuel lean conditions the formation of soot precursors such as benzene, naphthalene, phenanthrene and chrysene have a tendency to decrease when water is added to fuel. However, it decreases slowly with the increasing amount of water; where the 15 % water in fuel predicts the highest PAH precursor's concentrations but it is still lower than that of the pure fuel concentration; whereas the lowest concentration is found for 5 % water in fuel.

For higher equivalent ratio (i.e. fuel-rich), the peak temperature of PaSR model decreases, results in increasing the soot precursors formation as well as increasing the amount of un-burned fuel and that's would explain the tendency of the aromatic compounds to form soot particles at low temperature and fuel rich conditions.

This reduction is significant at 5% water in fuel which shows the lowest value, however it starts to increase slowly with the increasing amount of water in fuel up to 8% water, after that the formation tendency starts to increase and reaches the maximum at 15% water in fuel. Thus it is clear that; at fuel rich condition 'with more water in fuel' (i.e. 15% and above) the situation will be different and it may inversely affect the production rate of soot precursors.

### REFERENCES

- [1] M.S. Callén, M.T. de la Cruz, J.M. López, A.M. Mastral; PAH in airborne particulate matter. Carcinogenic character of PM10 samples and assessment of the energy generation impact Original Research Article Fuel Processing Technology, June 2010.
- [2] Göran Bengtsson, Niklas Törneman, Xiuhong Yang; Spatial uncoupling of biodegradation, soil respiration, and PAH concentration in a creosote contaminated soil, Environmental Pollution, Volume 158, Issue 9, P 2865-2871, 2865-2871, Sept. 2010.
- [3] Staci L. Massey Simonich, Oleksii Motorykin, Narumol Jariyasopit; PAH intermediates: Links between the atmosphere and biological systems, Chemico-Biological Interactions, Sept. 2010.
- [4] Khaiwal Ravindra, Ranjeet Sokhi, René Van Grieken; Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation, Atmospheric Environment, Volume 42, Issue 13, Pages 2895-2921, 2895-2921, April 2008.
- [5] Abhijeet Raj, Markus Sander, Vinod Janardhanan, Markus Kraft; A study on the coagulation of polycyclic aromatic hydrocarbon clusters to determine their collision efficiency Combustion and Flame, Volume 157, Issue 3, Pages 523-534, March 2010. Seung-Hyun Chung, Angela Violi; Peri-condensed aromatics with aliphatic chains as key intermediates for the nucleation of aromatic hydrocarbons Proceedings of the Combustion Institute, August 2010.
- [6] XI, J., Zhong, B.J., 'Review of Soot in Diesel Combustion Systems' School of Aerospace Engineering, Tsinghua University, Beijing 100084, China. Chemical Engineering Technology, 29, NO.6, 2006.
- [7] B.C. Choi, S.K. Choi, S.H. Chung; Soot formation characteristics of gasoline surrogate fuels in counterflow diffusion flames, Proceedings of the Combustion Institute, 2010.
- [8] Khaiwal Ravindra, Ranjeet Sokhi, René Van Grieken; Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation, Atmospheric Environment, Volume 42, Issue 13, Pages 2895-2921, 2895-2921, 2008.
- [9] M. P. Ashok and C. G. Saravanan; 'Performance and Emission of the Emulsified Fuel in a DI Diesel Engine Using Oxygenated Additive Diethyl Ether with Surfactant of Span-80', 21 (4), pp 1878-1882, Energy Fuels, 2007.
- [10] Siemiatycki, J., Dewar, R., Nadon, L., Gerin, M., Richardson, L., and Wacholder, S., Cancer and petroleum-derived liquids. Results from a case-referent study in Montreal. Scand J Work Environ Health 13, P 493-504, 1987.
- [11] Rosner, G., International Program on Chemical Safety Diesel Fuel and Exhaust Emissions, Environmental Health Criteria 171, Geneva, Report 1996.
- [12] Schlitt, H-G. and Exner, P., "Emission of diesel motors when run on alternative fuels", Glueckauf-Forschungshefte. Vol. 52, no. 6, pp. 278-282, 1991
- [13] M. Y. E. Selim & M. T. Ghannam; 'Combustion Study of Stabilized Water-in-Diesel Fuel Emulsion'; Energy Sources, Part A: Recovery, Utilization, and Environmental Effects V. 32, Issue 3, p 256-274, 2009
- [14] Xavier Tauzia, Alain Maiboom and Samiur Rahman Shah; 'Experimental study of inlet manifold water injection on combustion and emissions of an automotive direct injection Diesel engine'; Energy, Volume 35, Issue 9, Pages 3628-3639, 2010.
- [15] Y. Yoshimoto, T. Kuramoto, Z. Li, M. Tsukahara; 'Influence of Water Content Ratio on Combustion Fluctuation of Diesel Engine Using Emulsified Fuel'; Technical Paper of the JSME, Feb. 1998.
- [16] Samec, N, Kegl, B and Dibble, RW. 'Numerical and experimental study of water/oil emulsified fuel combustion in a diesel engine Fuel 81:2035-2044, 2002.



- [17] Zhenyu Tian, William J. Pitz, René Fournet, Pierre-Alexander Glaude, Frédérique Battin-Leclerc; 'A detailed kinetic modeling study of toluene oxidation in a premixed laminar flame, Proceedings of the Combustion Institute, 2010.
- [18] G.A.M. Janssen, 'Emissions of Diesel Engines Running on Different Biofuels and their Health Related Aspects' FACT Foundation. Horsten 1, 5612 AX, Eindhoven, The Netherlands, 2006.
- [19] Jonny Beyer, Grete Jonsson, Cinta Porte, Margaret M. Krahn; Freek Ariese Analytical methods for determining metabolites of polycyclic aromatic hydrocarbon (PAH) pollutants in fish bile: *Environmental Toxicology and Pharmacology*, Volume 30, Issue 3, Pages 224-244, 2010.
- [20] Bartok, W. and A. F. Sarofim. Eds. *Fossil Fuel Combustion: a Source Book*. John Wiley & Sons, Inc., New York, 1991.
- [21] Hall, R. E., 'Effect of water/residual oil emulsions on air pollutant emissions and efficiency of commercial boilers', Environmental Protection Agency, Research Triangle Park, NC, ASME J. Eng. Power; Vol/Issue: 98:4; P 425-434, 1976.
- [22] M. P. Ashok and C. G. Saravanan, 'Combustion Characteristics of Compression Engine Driven by Emulsified Fuel Under Various Fuel Injection Angles', *J. Energy Resour. Technol*, Volume 129, Issue 4, 325 (7 pages), 2007.
- [23] Nageli, D. W. and Moses, C. A., 'A correlation for soot formation in turbine combustion that includes emulsified fuels', in Proc. of Symp. on Water-in-Fuel Emulsions in Combustion, ed. R. Walter and J. White. U.S. Department of Transportation, Report No. CG-D-12-78, 1978.[25] Lawson, A, Vergeer, E.C., Mitchell, E.W. and Dainty, E.D., "Heavy-Duty Diesel Emission Control", *A Review of Technology*, vol. 36. Montreal, Quebec, Canada: CIM; p. 238, 1986.
- [24] Radloff, E. and Gautier, C., 'Diesel Engine NOX reduction Using Charge Air Water Injection', Transportation Development Centre Transport Canada Proceedings of ICED of ASME: 2005 Fall Technical Conference, Ottawa, Canada, ICEF2005-1235, Sept. 11-14, 2005.
- [25] Heena V. Panchasara, Benjamin M. Simmons, Ajay K. Agrawal, Scott K. Spear and Daniel T. Daly; 'Combustion Performance of Biodiesel and Diesel-Vegetable Oil Blends in a Simulated Gas Turbine Burner', *J. Eng. Gas Turbines Power*, Volume 131, Issue 3, 031503 (11 pages), 2009.
- [26] Massimiliano Di Domenico, Peter Gerlinger, Manfred Aigner; Development and validation of a new soot formation model for gas turbine combustor simulations *Original Research Article Combustion and Flame*, Volume 157, Issue 2, P 246-258, 2010.
- [27] Curran, H. J., Pitz, W. J., and Westbrook, C. K., 'Extinction and Autoignition of n-Heptane in Counterflow Configuration", *Proceedings of the Combustion Institute*, Volume 28, p. 2029-2037, 2002 UCRL-WEB-204236 Review and release date: May 19, 2004.
- [28] Zhou P.L., Thorp I. 'Marine diesel engine emissions and their control', Department of Marine Technology, University of Newcastle upon Tyne, United Kingdom, 1997.
- [29] Yoshimoto, Y., Tsukahara, M., Murayama, T., 'Studies on the microexplosion of emulsified fuels', *Trans. JSME (B)* 89-0059 B, 1989.
- [30] Lasheras, J.C., Fernandez-Pello, A.C. and Dryer, F.L. 'Experimental observations on the disruptive combustion of free droplets of multicomponent fuels'. *Combustion Science Technology*. Vol. 22, pp. 195-209. 1980.
- [31] Spadaccini, L. J. and Pelmas, R., in Symp. On Vaporation and combustion of fuel droplets", American Chemical Society, Div. of Petroleum Chem. San Francisco Meeting, August 29- Sept. 3, 1976.
- [32] Chang Sik Lee, Sung Wook Park and Sang Il Kwon; 'An Experimental Study on the Atomization and Combustion Characteristics of Biodiesel-Blended Fuels', *Energy Fuels*, 19 (5), pp 2201-2208, July 27, 2005.
- [33] Tamjima, H and Takasaki, K and Goldsworthy, L and Taskaishi, T, Diagnosis of combustion with water injection using high-speed visualization and CFDs', In: THIESEL International Conference on Thermo- and Fluid Dynamic Processes in Diesel Engines, 7 - 10, Valencia, Spain, 2008.
- [34] Hyun Kyu Suh, Hyun Gu Roh, and Chang Sik Lee, ' Spray and Combustion Characteristics of Biodiesel Diesel Blended Fuel in a Direct Injection Common-Rail Diesel Engine', *J. Eng. Gas Turbines Power*, Volume 130, Issue 3, 032807 (9 pages), 2008.
- [35] Yung-Sung Lin and Hai-Ping Lin; 'Spray characteristics of emulsified castor biodiesel on engine emissions and deposit formation', *Renewable Energy*, Volume 36, Issue 12, P. 3507-3516, 2011.
- [36] XI, J., Zhong, B.J., 'Review of Soot in Diesel Combustion Systems' School of Aerospace Engineering, Tsinghua University, Beijing 100084, China. *Chemical Engineering Technology*, 29, NO.6, 2006.
- [37] Miller, J.A., Kee, R.J. and Westbrook, C.K. 'Chemical Kinetics and Combustion Modeling'. *Annual Review of Physical Chemistry*, Vol 41:345-387, 1990.
- [38] Abhijeet Raj, Peter L.W. Man, Tim S. Totton, Markus Sander, Raphael A. Shirley, Markus Kraft; New polycyclic aromatic hydrocarbon (PAH) surface processes to improve the model prediction of the composition of combustion-generated PAHs and soot; *Carbon*, Volume 48, Issue 2, Pages 319-332, 2010.
- [39] Glassman, I., Soot formation in combustion processes. 22nd Symposium (International) on Combustion, The Combustion Institute, Pittsburgh (USA), 295-311, 1988.
- [40] Lidong Zhang, Jianghuai Cai, Taichang Zhang, Fei Qi; Kinetic modeling study of toluene pyrolysis at low pressure *Combustion and Flame*, Volume 157, Issue 9, Pages 1686-1697, 2010.
- [41] Onwudili, J.A., Williams, P.T., "Reaction mechanisms for the decomposition of phenanthrene and naphthalene under hydrothermal conditions", Energy and Resources Research Institute, The University of Leeds, Leeds LS2 9JT, UK, The journal of supercritical fluids, 2006.
- [42] Violi, A., D'Anna, A., D'Alessio, A., "Modeling of particulate formation in combustion and pyrolysis", *Chemical Engineering Science*, 54, 3433-3442, 1999.
- [43] A. H. El-Sinawi; Water- Surrogate Fuel Emulsion Combustion Effect on CO and NOx Emissions, *Int. J. of Thermal & Environmental Engineering* Volume 1, No.2, P 99-108, 2010.