Proceedings of the 6th International Conference of Fluid Flow, Heat and Mass Transfer (FFHMT'19)
Ottawa, Canada – June, 2019
Paper No. FFHMT 170
DOI: 10.11159/ffhmt19.170

Diffusion Coefficient of Ethanol – Gasoline Blends in Air

Isam Al Zubaidi, Sheegal Madavana Govindan, Cody Enns, Michael Reiger, Tianci Li
Industrial Systems Engineering, Faculty of Engineering and Applied Science, University of Regina
3737 Wascana Parkway, Regina, SK, Canada
Isam.Al.Zubaidi@uregina.ca

Abstract **-** Vapor diffusion was studied from volatile liquids of ethanol blend gasoline. The studying was conducted at two operating temperatures of 40 and 50 oC and blending of 0, 5, 10, 20, 30, 40, and 100 % by volume ethanol. The diffusion coefficients of the blend showed an increase in diffusion coefficient in air with increasing temperature and % of ethanol added. The diffusivity coefficient of gasoline –ethanol followed the following polynomial equations:

Deff = 2E-05(% vol. ethanol)2 +7E-07 (% vol. ethanol) +5E-10 { at 40 oC}
Deff = 5E -06(% vol. ethanol) - 1E-06((% vol. ethanol) + 2E-07 { at 50 oC)

The diffusion coefficient of the blend in both operating temperatures was increased sharply after the addition of 20% by volume of ethanol.

Keywords**:** Gasoline, Ethanol blending, Diffusion.

1. Introduction

Gasoline is a refined product from crude oil. It is a mixture of different hydrocarbons. It is considered a volatile or has high tendency to vaporize, and this is will allow easy starting and drivability when the engine is cold. Extremely high volatility of gasoline will fail in combustion process inside the engine because of converting the liquid to vapor in the fuel line and this is regarded as a vapor lock. Gasoline might evaporate from fuel tank in hot climate and diffuse in air and this will affect the health and environment. Refineries control and regulate the vapor pressure of gasoline by distillation. Gasoline in the United States contains up to 10% ethanol by volume (E10); although Environmental Protection Agency (EPA) has already begun allowing to produce E15 [1]. This may increase the amount of blending ethanol to gasoline. In Canada some provinces allow to have up to 10% ethanol. The use of ethanol in gasoline has become a worldwide tendency to reduce the net CO_2 emissions to the atmosphere, increasing gasoline octane rating, and reducing dependence on petroleum products [2]. Ethanol has higher heat of vaporization than gasoline (Table1) [3]. This makes the temperature of the intake manifold lower, which increases air-fuel mixture density and increasing the engine's volumetric efficiency. This will cause lower combustion temperatures and burning velocities, which could potentially cause higher CO and HC emissions. From Table 1, it is clear that the Reid Vapor Pressure (RVP) is much lower than that of gasoline, and this will lower VOCs emissions during pumping processes.

Table 1: Properties of ethanol-gasoline blends.

Property	Gasoline	E10	E20	E100
Density, Kg/m^3	733	739	746	790.7
LHV, Kj/kg	43000	41282	39591	26950
Latent heat of vaporization, kj/kg	305			840
RVP, KPa	62			14
RON	88.5	90.7	94.8	115
MON	80.3	81.6	83.3	102
AKI, AKI=(RON+MON)/2	84.4	86.2	89.1	108.5
Stoichiometric air/fuel ratio	14.49	13.89	13.31	8.87

The vapor pressures of high-octane gasoline varied with temperature. The vapor pressure is s increasing with temperature. The enthalpy of vaporization can be calculated using Clausius–Clapeyron equation for the evaporation process:

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2} \qquad (1)$$

where p is the vapor pressure at temperature T; ΔH_{vap} is the enthalpy of vaporization (supposed to be constant). The plot of the logarithm of ethanol–gasoline mixture vapor pressure versus inverse thermodynamic temperature can be estimated [4]. The straight line was obtained from the plot of the logarithm of vapor pressure against the reciprocal of the absolute temperature. The enthalpy of vaporization is changed with % ethanol content [5 and 6]. Maximum vapor pressure occurs with 20% ethanol-gasoline blend at which a positive azeotrope is formed [2]. The trend is different in enthalpy of vaporization. Such a trend is true up to 20%; the value then decreases a little and appears to flatten out between E30 and E60. After E60, it begins to increase again. New restriction regulations were applied for gasoline particulate matter emission from spark- ignited engines and increasing ethanol content in gasoline. Ethanol addition leads to limit particulate emissions. It has a positive effect on exhaust NOx emission reduction. For higher loads, exhaust CO emissions are reduced with ethanol addition. Ethanol addition improves combustion robustness to spark advance, start of injection timing and spark plug penetration in the combustion chamber. However, when decreasing load and engine speed, ethanol has a negative effect on the indicated efficiency. This is due to enhanced wall heat transfers with ethanol blends since a longer spray penetration may lead to combustion closer to the walls of the combustion chamber [6]. Biofuel is ethanol–gasoline blend. High octane number of ethanol makes it a high knock resistant fuel [7]. Due to ethanol's high sensitivity, knock-limited performance improved to a much greater extent with increasing ethanol content as combustion phasing was retarded. Increasing ethanol content increased the knock-limited performance before enrichment was required to control exhaust gas temperature. The RON ratings of the fuels did not fully reflect the observed knock resistance of mid-to-high level ethanol blends (E20 and higher). Biofuel has a profound effect on the evaporation characteristics of the mixture. Thermodynamic properties of the blends can be significantly different than the constituents. The clear understanding of the biofuel properties is important to optimize engine design [8]. Most biofuel work is related to PM and low ethanol blend percentages (<20 vol. %). Ethanol was shown to reduce the aromatic species in an ethylene premixed flame for concentrations up to 10% by mass [9-11]. However, in non-premixed ethylene flames, the ethanol addition increasing soot production for the same concentrations [12,13]. Similar observation was shown by [7]. Increasing soot formation for low concentration ethanol blends with ethylene in a counter-flow diffusion flame but saw a decrease when the ethanol content exceeded 20% by mass. Similar results were found with higher hydrocarbons. The increasing of benzene in a counter- flow diffusion propane flame with 10% ethanol addition by volume, followed by a decrease when ethanol concentration was increased to 15% [14-15]. Experiments with toluene, isooctane, n-heptane, and gasoline showed similar trends [16–20]. There are many benefits of adding ethanol to gasoline to be a biofuel. It reduces net CO_2 emissions to the atmosphere, increasing gasoline octane rating and reducing dependence on petroleum products although many problems achieved with this addition such as the corrosivity of ethanol when there is a contact with certain materials in fuel storage and delivery systems including some rubber compounds and zinc and aluminum alloys which used in the carburetors. Ethanol can dry out the rubber components in a fuel system which can lead to cracking and brittle fuel lines, floats, seals and diaphragms. Ethanol is hygroscopic material. Water can enter fuel containers during filling up. This may cause corrosion of internal parts. Ethanol can act as solvent which dissolve the varnish and other deposits in tanks and lines [21]. This material can clock the fuel injection system. The air pollution information for ethanol gasoline blends is shown in [21 and 22]. This work shown that carbon monoxide is decreased for E10 and then no further improvement for E15 and E20. It reduces the ability of blood to carry oxygen to body tissues and vital organs; aggravation of heart disease. The Particulate matter is significant increases due to corn ethanol production compared to conventional gasoline. The particular matter has an effect on aggravation of respiratory and cardiovascular disease; decreased lung function; increased asthma; premature death; environmental influence: impairment of visibility, effects on climate.

Molecular diffusion is defined as the random motions of molecules through different fluids which finally forming homogenous mixture. Usually, according to mass transfer phenomena, diffusion occurs from high concentration regions to low concentration regions. Many factors are affecting diffusion such as temperature, pressure and molecular weight of the material. Diffusion becomes faster at high temperature, low pressure, and low molar mass. The diffusivity of the vapor of a volatile liquid in air can be conveniently determined by Winklemann's method in which liquid is contained in a vertical capillary tube, maintained at a constant temperature, and an air steam is passed over the top of the tube to ensure that the partial pressure of the vapor is transferred from the surface of the liquid to the air stream by molecular diffusion. The rate of mass transfer is given by [23] and [24]:

$$N_A = D\left(\frac{C_A}{L}\right)\left(\frac{C_T}{C_{BM}}\right) \tag{2}$$

Considering the evaporation of the liquid:

$$N_A = \left(\frac{\rho_L}{M}\right)\frac{dL}{dt} \tag{3}$$

Thus

$$\left(\frac{\rho_L}{M}\right)\frac{dL}{dt} = D\left(\frac{C_A}{L}\right)\left(\frac{C_T}{C_{BM}}\right) \tag{4}$$

Integrating and putting $L=L_o$ at $t=0$

$$L^2 - L_o^2 = \left(\frac{2MD}{\rho_L}\right)\left(\frac{C_A C_T}{C_{BM}}\right)t \tag{5}$$

$L-L_o$ can be measured accurately using the electronic microscope.
$(L-L_o)$ at time t = is the difference in height of the level between the initial level and level at any time t.

$$(L-L_o)\ (L-L_o+2L_o) = \left(\frac{2MD}{\rho_L}\right)\left(\frac{C_A C_T}{C_{BM}}\right)t \tag{6}$$

Rearranging to solve for $\frac{t}{L-L_o}$

$$\frac{t}{L-L_o} = \left(\frac{\rho_L}{2MD}\right)\left(\frac{C_{BM}}{C_A C_T}\right)(L-L_o) + \left(\frac{\rho_L c_{BM}}{MD\ C_A C_T}\right)L_o \tag{7}$$

If m is the slope of the graph of $\frac{t}{L-L_o}$ versus $(L-L_o)$, then:

$$D = \left(\frac{\rho_L C_{BM}}{2mMC_A C_T}\right) \tag{8}$$

Diffusion coefficients, along with other parameters, are required inputs to some environmental transport or risk assessment models [25]. Diffusion coefficients of ethanol-gasoline blends are not available in any literature at any temperature.

The objectives of this work is to examine the effect of the addition of ethanol to gasoline on the diffusivity of the blend in air at different ethanol concentrations and operating temperatures.

2. Experimental work

2. 1. Material

Gasoline free of ethanol was collected locally with octane number of 91 has the following properties.

Table 2: Properties of Gasoline.

Property	
Appearance	Red, Yellow or colorless liquid
Octane No.	91
Ethanol content	Zero%
Specific gravity at 15/15 ºC	0.73254
Kinematic viscosity @40 ºC, cSt	0.719
Vapor pressure@38 ºC, KPa	78
Flash Point	< -40 °C
Boiling Point	35 - 210 °C
Upper explosion limit	8 %(V)
Lower explosion limit	1 %(V)
Auto-ignition temperature	> 250°C/482°F

Ethanol was bought from Sigma Aldrich with 98% purity. It is used without any further purification. Ethanol was added to gasoline by volume to have E0, E5, E10, E20, E30, E40, and E100.

2. 2. Equipment setup

Gaseous diffusion coefficient measurement apparatus was used. This equipment utilizes a high definition digital microscope linked to a PC to observe and measure the movement of the phase boundary of the liquid inside a capillary tube as the liquid diffuses into stationary air. Gasoline sample, contained inside a capillary tube, is maintained at a constant temperature by a PID controlled heated metal block. The block is heated by an electric cartage heater and kept at a constant temperature using an electrical control loop. The air is passed across the top of the capillary tube creating partial pressure difference between the gasoline sample surface and the following air stream. As the gasoline sample vapor from the liquid phase into the air stream, the amount of liquid is reduced and the phase boundary between the liquid and the air drops. Measurement the change in phase boundary with time will allow the molar mass transfer rate to be measured. A slot in the heated block allows the phase boundary to be observed using a high definition microscope. This microscope produces high definition images onto a standard windows computer. The software provided with the microscope includes high accurate measurement and an automated time laps facility either as video or multiple still images. The schematic diagram of the gaseous diffusion is shown in Figure 1.

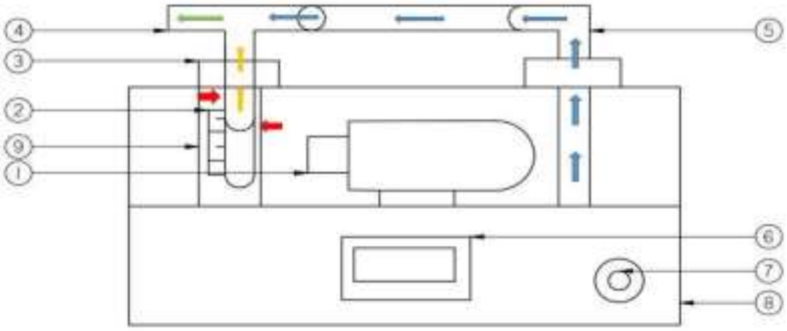

Fig. 1: Gas diffusion apparatus.

(1) High definition USB microscope, (2) Measuring tool, (3) heater block, (4) capillary tube, (5) Air pumping to the capillary tube to allow diffusion of gasoline vapor in air to occur, (6) front display gauge and heater temperature controller, (7) power switch, (8) fan, to allow air through the capillary tube, (9) 25-watt electrical controller heater.

3. Discussion

The graphs of $\frac{t}{L-L_o}$ versus (L-L$_o$) of all gasoline-ethanol mixtures at operating temperature 50 ^{o}C were plotted. The plot for pure gasoline at 50 ^{o}C is shown in Figure 2. The parameters required to calculate the diffusion coefficient are shown in Table 3.

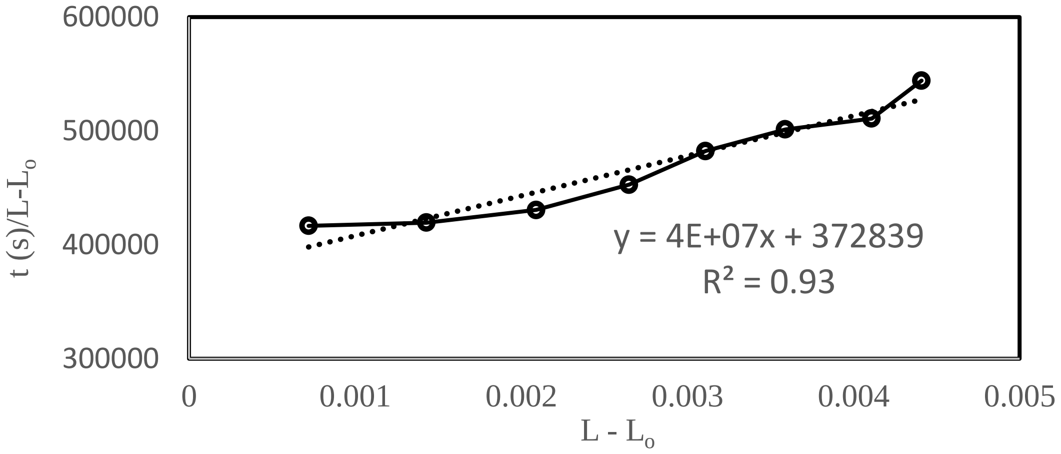

Fig. 2: $\frac{t}{L-L_o}$ $vs. L - Lo\ for$ pure gasoline at 50 ^{o}C.

Table 3: Diffusion coefficient calculation for pure gasoline at 50 ^{o}C.

Property	
Density of gasoline, (Kg/m^3)	732.54
Molecular weight, (Kg/Kmole)	105
Pressure, KPa	101.325
Gas constant (R), (kJ /kmole. K)	8.314
Temperature, K	323.15
C_T , kmole/m^3	0.03894

CA , kmole/m^3	0.018908
CB1, kmole/m^3	0.018908
CB2, kmole/m^3	0.018805
CBM,	0.018569
α	4 x10^7
D, m^2/s	2.306 x10^{-7}

The diffusivity coefficient of gasoline (ON 91) and pure ethanol at 40 ^{o}C and 50 ^{o}C is shown in Figure 3. This shown that the diffusion coefficient of ethanol is higher than gasoline.

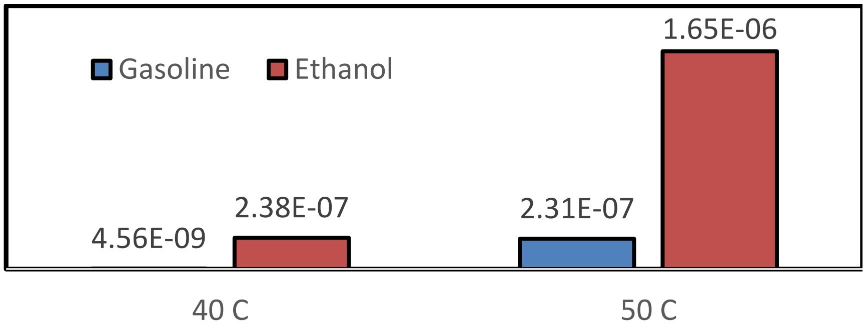

Fig. 3: Diffusion coefficient of gasoline 91 and pure ethanol at 40 and 50 ^{o}C.

The vapor pressure of blend was collected from [4 and 6] at 20 ^{o}C and the heat of vaporization was measured. The Clausius–Clapeyron equation was applied to find the vapor pressure of blend at 40 ^{o}C and 50 ^{o}C. The diffusion coefficient of gasoline-ethanol blend at 40 ^{o}C and 50 ^{o}C are shown in Figure 4 and 5 respectively.

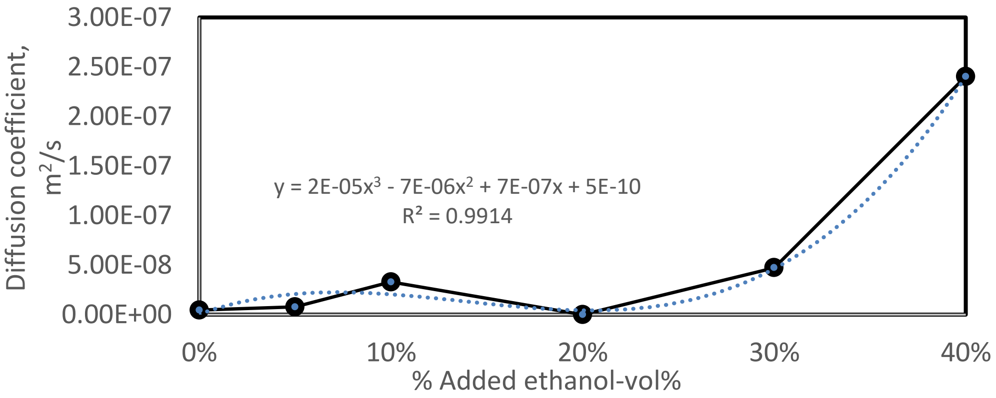

Fig. 4: Changes in diffusion coefficient of gasoline with % by vol ethanol at 40 ^{o}C.

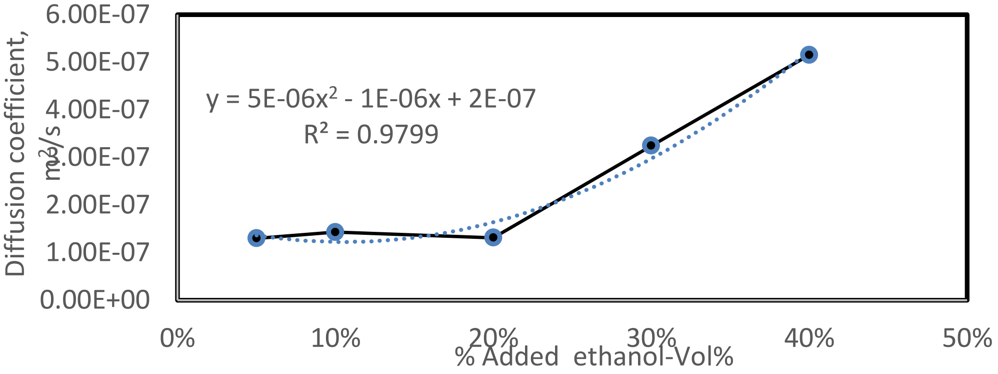

Fig. 5: Changes in diffusion coefficient of gasoline with % by vol ethanol at 50 °C.

The diffusion coefficient of gasoline-ethanol blend curve at 40 °C is fitted to polynomial of order 3 and at 50 °C followed the polynomial order 2 as follow:

D_{eff} = 2E-05(% vol. ethanol)^2 +7E-07 (% vol. ethanol) +5E-10 { at 40 °C}
D_{eff} = 5E -06(% vol. ethanol) - 1E-06((% vol. ethanol) + 2E-07 { at 50 °C)

It is believed that the diffusion coefficient of ethanol –gasoline blend is increased at 20% ethanol. It is in concise with the work of other authors that the maximum allowable ethanol is 20 vol % because above this value more diffusion in air will occur which may contaminate the polluted area of air. The addition of ethanol is increasing the vapor pressure of the blend and above 20% of ethanol addition may leads to vapor lock in fuel line of the engine and this will reduce the performance of the combustion process of the fuel.

4. Conclusion

Diffusion coefficient and other properties of gasoline –ethanol blends play an important rule to some environmental transport or risk assessment. It is believed that it is important to include this property to other properties. The diffusivity coefficient of the blend increased with the addition of ethanol as well as the climate temperature.

Acknowledgement

The authors would like to thank Industrial System Engineering / Faculty of Engineering and Applied Science/ University of Regina for providing all the facilities to perform this work.

Nomenclature:

C_A	Saturation conc. at interface [kmol/m^3]
C_{BM}	Logarithmic mean molecular conc. of vapor [kmol/m^3]
C_T	Total molar conc.= C_A+ C_{BM} [kmol/m^3]
D	Diffusivity or diffusion coefficient [m^2/s]
L	Effective distance of mass transfer [mm]
M	Gasoline Molecular Weight = 58.08 kg/mol
P_v	Gasoline vapor pressure (at 40°C) = 56kN/m^2
P_a	Atmospheric Pressure = 101.3 KPa
T	Time (s)
T_{abs}	Absolute Temperature = 273
T_a	Temperature of gasoline in water bath
ρ_L	Liquid Acetone density (at 40°C) = 790 kg/m^3

References

[1] EPA, Ethanol Waivers (E15 and E10), *Environmental Protection Agency*, 2011.

[2] J. E. Tibaquirá, J. I. Huertas , S. Ospina, L. F. Quirama and J. E. Niño, "The Effect of Using Ethanol-Gasoline Blends on the Mechanical Energy and Environmental Performance of In-Use Vehicles," *Energies*, vol. 11, pp. 221, 2018.

[3] R. M. Balabin, R. Z. Syunyaev, S. A. Karpov, "Molar enthalpy of vaporization of ethanol–gasoline mixtures and their colloid state," *Fuel*, vol. 86, pp. 323-327, 2007.

[4] L. Chen and R. Ston, "Measurement of Enthalpies of Vaporization of Isooctane and Ethanol Blends and Their Effects on PM Emissions from a GDI Engine," *Energy Fuels*, vol. 25, pp. 1254-1259, 2011.

[5] R. A. Stein, D. Polovina, K. Roth, M. Foster, M. Lynskey, T. Whiting, J. E. Anderson, M. H. Shelby, T. G. Leone, S. V. Griend, "Effect of Heat of Vaporization, Chemical Octane, and Sensitivity on Knock Limit for Ethanol - Gasoline Blends," *SAE Int. J. Fuels Lubr.*, vol. 5, no. 2, pp. 823-843, 2012.

[6] M. Salamanca, M. Sirignano, A. D'Anna, "Particulate formation in premixed and counter-flow diffusion ethylene/ethanol flames," *Energy Fuels*, vol. 26, pp. 6144-52, 2012.

[7] K. H. Song, P. Nag, T. A. Litzinger, D. C. Haworth, "Effects of oxygenated additives on aromatic species in fuel-rich, premixed ethane combustion: a modeling study," *Combust Flame*, vol. 135, pp. 341-349, 2003.

[8] J. Wu, K. H. Song, T. Litzinger, S.-Y. Lee, R. Santoro, M. Linevsky, "Reduction of PAH and soot in premixed ethylene–air flames by addition of ethanol," *Combust Flame*, vol. 144, pp. 675-87, 2006.

[9] S. Yakimov, D. Knyaz'kov, T. Bol'shova, A. Shmakov, O. Korobeinichev, F. Qi, "Investigation of the effect of ethanol additives on the structure of low-pressure ethylene flames by photoionization mass spectrometry," *Combust Explo. Shock Waves*, vol. 48, pp. 609–619, 2012.

[10] C. S. McEnally, L. D. Pfefferle, "The effects of dimethyl ether and ethanol on benzene and soot formation in ethylene nonpremixed flames," *Proc Combust Inst*, vol. 31, pp. 603-610, 2007.

[11] K. L. McNesby, A. W. Miziolek, T. Nguyen, F. C. Delucia, R. R. Skaggs, T. A. Litzinger, "Experimental and computational studies of oxidizer and fuel side addition of ethanol to opposed flow air/ethylene flames," *Combust Flame*, vol. 142, pp. 413–427, 2005.

[12] M. Salamanca, M. Sirignano, M. Commodo, P. Minutolo, A. D'Anna, "The effect of ethanol on the particle size distributions in ethylene premixed flames," *Exp Thermal Fluid Sci*., vol. 43, pp. 71–75, 2012.

[13] L. Rubino, M. J. Thomson, "The effect of oxygenated additives on soot precursor formation in a counter flow diffusion flame," *SAE Technical Paper*, 1999.

[14] A. Alexiou, A. Williams, "Soot formation in shock-tube pyrolysis of toluene, toluene-methanol, toluene-ethanol, and toluene-oxygen mixtures," *Combust Flame*, vol. 104, pp. 51–65, 1996.

[15] I. Frenzel, D. Trimis, "Study on the influence of ethanol addition on exhaust gas composition and soot formation in iso-octane flames," in *Proceedings of the European Combustion Meeting*, 2015.

[16] F. Inal, S. M. Senkan, 2002, Effects of oxygenate additives on polycyclic aromatic hydrocarbons (PAHs) and soot formation," *Combust Sci Technol*, vol. 174, pp. 1-19, 2002.

[17] R. Lemaire, E. Therssen, P. Desgroux, "Effect of ethanol addition in gasoline and gasoline–surrogate on soot formation in turbulent spray flames," *Fuel*, vol. 89, pp. 3952-3959, 2010.

[18] Richard Russell, "The problem with ethanol in gasoline," Globe and Mail Inc. Toronto, ON Canada, Phillip Crawley, Publisher, 2019.

[19] M. M. Maricq, "Soot formation in ethanol/gasoline fuel blend diffusion flames," *Combust Flame*, 2012.

[20] American Lung Association. (2009). Testimony of A. Blakeman Early presented on behalf of the American Lung Association before the Senate Environment and Public Works Committee Subcommittee on Clean Air and Nuclear Safety [Online]. Available: http://epw.senate.gov/public/index.cfm?FuseAction=Hearings.Hearing&Hearing_ID=3fdd18ff-802a- 23ad-4378-d21b6beb4d5a

[21] O. V. Naidenko. (2009). "Ethanol-Gasoline Fuel Blends May Cause Human Health Risks and Engine Issues," EWG: The power of information, Environmental working group [Online]. Available: www.ewg.org

[22] E. L. Cussler, *Diffusion & Mass Transfer in Fluid Systems*. Cambridge University Press, pp. 62-65, 1984.
[23] R. E. Treybal, *Mass Transfer Operations*. 3rd Ed., Chapter 2, McGraw-Hill, New York, 1980.
[24] EPA On-line Tools for Site Assessment Calculation, “Modeling Subsurface Petroleum Hydrocarbon Transport” [Online]. Available: http://www.epa.gov/athens/learn2model/part-two/onsite/estdiffusion.htm
[25] D. H. Qi, C. F. Lee, “Combustion and emissions behavior for ethanol–gasoline blended fuels in a multipoint electronic fuel injection engine,” *International Journal of Sustainable Energy*, vol. 35, no. 4, pp. 323-338, 2016.