Numerical Study of Nitrogen Oxides (NO_x) Formation in High-Pressure Diffusion Flames of Methane, Methanol and Methyl Formate

J. M. Ngugi, P. N. Kioni, and J. K. Tanui

***Abstract*—The effects of pressure on NO_x formation and flame structures in diffusion flames of methyl formate is investigated. The flames are simulated from the conservation equations for mass, momentum, energy, chemical species and equation of state. The results obtained, are validated by comparison with results obtained from the extensively studied methane/air and methanol/air flames. A fully infinite computational domain between two opposed nozzles (one ejecting pure fuel and the other pure air) has been used for all the flames. The initial temperature of both fuel and air streams is taken as 300 K. The flames have been computed at constant pressures of 1 atm and 50 atm and at a strain rate of 30 s-1. It has been observed that pressure affects the structure of flames and formation of various species including oxides of nitrogen in diffusion combustion of CH_4, CH_3OH and CH_3OCHO. It has also been shown that in diffusion flames NO formation in the three fuels increases with increase in pressure. A comparison of N, HCN, N_2O, CH, O, OH and N_2 has shown that NO formation in diffusion flame mainly occurs through the reaction $N_2 + O \rightarrow NO + N$, which is a thermal-NO formation route. Finally, it is established that increase in pressure results to reduction in flame thickness due to the high rate of heat release at high pressures.**

***Index Terms*—Methane, methanol, methyl formate, nitric oxide, diffusion flame, thermal-NO.**

I. Introduction

The reduction in reserves of fossil fuels and the need to reduce environmental pollution has promoted the development of renewable and alternative fuels. Biodiesel fuels (methyl esters fuels) has been investigated as alternative transportation fuels because of their ability to reduce the emissions of CO, particulate matter and unburnt hydrocarbons as noted by Basha and Gopal [1]. Liu *et al.* [2], showed that biodiesel fuels give higher thermal efficiencies than diesel at various engine speeds. Biodiesel fuels typically contain about 10-15 % or greater oxygen content by mass. The presence of oxygen atom in the structure of the biodiesel fuel makes the fuel to burn more efficiently with reduced emissions of soot, unburnt hydrocarbons and carbon monoxide [3]. However, as noted by Michael *et al.* [4] and Magin *et al*. [5], combustion of biodiesel fuels produces more nitrogen oxides (NO_x) compared to fossil fuels. NO_x are pollutants whose reduction is a major issue in the design of combustion devices. The purpose of the study reported herein is to determine the NO_x formation mechanism in the combustion of esters.

Biodiesel is produced from vegetable oils through a transesterification process. The alcohol commonly used in this process is methanol. For this reason, most common bio-diesel fuels are methyl-esters. Typical biodiesel consists of mixtures of saturated and unsaturated long-chain fatty acid methyl-esters with 15-20 or more carbon atoms in their alkyl chain. The chemical kinetics involved in combustion of these large ester species are complex due to the formation of many intermediate species. This makes the computations involved during kinetic modeling of real fuels more difficult to analyze. Hence, fuels of simpler chemical structure, referred to as surrogate fuels, are used to approximate or represent processes involved in the combustion of these real fuels, as reported by Dooley *et al.* [6], [7] and Francisco [8]. In this regard, esters with a low number of carbon atoms are adopted as surrogate fuels. The simpler structure is amenable to more detailed chemical kinetics study.

To this end, methyl formate (CH_3OCHO), the smallest methyl ester molecule, is well suited for the studies of esters and hence biodiesel. In this regard, also, methane (CH_4) is a suitable representative of fossil fuels, viz., hydrocarbon fuels for the purpose of determining the influence of oxygenation on NOx formation. Methanol (CH_3OH) chemical species appears quite prominently in the CH_3OCHO detailed chemical kinetics. Furthermore, it is used in transesterification and has one carbon chemical structure comparable to that of methyl formate and methane. There is a lot of data, experimental, theoretical and numerical, on oxidation of CH4 and CH3OH and this provides a good basis for further studies incorporating NO_x formation mechanism, and for validating the solution obtained in new studies.

CH_3OCHO has been a subject of various experimental and kinetic modeling studies that have mainly focused on decomposition pathway, development of kinetic modeling parameters and species formation. Dooley *et al*. [6] reported a detailed oxidation mechanism of methyl formate. This mechanism is based on experimental data obtained from flow reactor studies, shock tube ignition delays and laminar burning velocity. Dooley *et al.* [7] have also reported oxidation of methyl formate in a series of burner stabilized laminar flames at low-pressures of 0.03-0.04 bar and fuel-air equivalence ratios from 1.0 to 1.8. The kinetic mechanism did not incorporate NO_x formation.

Most combustion chemistry studies have focused on normal pressures, viz., 1 atmosphere, much lower than the typical pressure range of 20-50 atm experienced in internal combustion engines. Thus, better insight of the NO_x

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formation may be obtained by simulating combustion at these higher pressures. This requires the knowledge of high pressure rate constants and/or the dependence of rate constants on pressure.

According to Dooley *et al.* [6], the computation of the high pressure rate constant, the dependence of rate constant on pressure and the determination of collision energy transfer parameter are the major uncertainties in kinetic modeling of methyl formate flames. Either Quantum-Rice-Ramsperger-Kassel (QRRK) or Rice-Ramsperger-Kassel-Markus (RRKM) theory (Dooley *et al.* [6]) may be applied to estimate the rate constant at higher pressure combustion. Metcalfe *et al*. [9] computed pressure dependent rate constants for methyl formate decomposition using Rice-Ramsperger-Kassel-Markus (RRKM) theory. Dooley *et al.* [6] evaluated the performance of QRRK and RRKM high pressure rate constants for the major methyl formate decomposition channel, $CH_3OCHO \Leftrightarrow CH_3OH+CO$ against methanol measurement and observed that the QRRK rate parameters give peak methanol values that are very close to the peak experimental values.

Oxidation of methane at high pressures has been investigated by various researchers Hunter *et al.* [10], Petersen *et al.* [11], Sibendu *et al.* [12] and Curran [13]. Thomsen *et al.* [14], modeled NO formation in premixed, high-pressure methane flames and showed that GRI-Mech 2.11 mechanism is not suitable for the quantitative prediction of NO concentrations in rich, premixed flames. Sibendu *et al.* [12] used three different mechanisms namely GRI-Mech 2.11, GRI-Mech 3.0 and the San Diego mechanism to investigate the effect of pressure on flame structure. At normal pressures, there was agreement for all the mechanisms between the simulations and the experiments. However, beyond a critical pressure of 11 bar, the structure and temperature profiles of the premixed flame changed significantly [12]. Rozenchan *et al.* [15], reported numerical and experimental investigation of laminar burning velocities and chemical effects of methane/oxidizer flames up to 60 atm. Simulations using GRI Mech 3.0 in this case showed satisfactory agreement with experimental data up to 20 atm and moderate deviation for pressures above 40 atm. Petersen *et al.* [11] investigated methane/oxygen ignition at elevated pressures (40-260 atm) and intermediate temperatures (1040-1500 K) and various equivalence ratios. Reactions involving HO_2, CH_3O_2 and H_2O_2 were identified as major reactions needed to model methane oxidation at conditions of high pressure and intermediate temperatures.

Alcohols such as methanol and ethanol are currently used as alternative fuels or as additives to transportation fuels to improve performance. Held and Dryer [16] developed a comprehensive detailed mechanism for methanol oxidation. This mechanism has been validated against multiple experimental data sets: flow reactor, static reactor, shock tube, premixed flame experiments and counter flow diffusion flames. The mechanism covers conditions of temperature from 633 to 2050 K, pressure from 0.26 to 20 atm and equivalence ratios from 0.05 to 2.6. In Sheng *et al.* [17], the pressure and temperature dependent rate constants were obtained by utilizing QRRK theory over a pressure range of 0.01-100 atm and temperature range of 250-2500 K.

Nitrogen oxides NOx are composed of nitric oxide, NO and nitrogen dioxide NO_2. The four main routes of NO formation in combustion processes are Zel'dovich mechanism (thermo NO), N_2O route, prompt-NO and Fuel Bound Nitrogen (FBN). Thermo NO is formed in high temperature flame regions through extended Zel'dovich mechanism which is shown below.

$$N_2 + O \leftrightarrow NO \quad (1)$$

$$N + O \leftrightarrow NO + O \text{ and} \quad (2)$$

$$N + OH \leftrightarrow NO + H \quad (3)$$

Prompt-NO is formed at low temperature flame front regions due to the presence of CH radicals. The CH radical reacts with molecular nitrogen according to Eq. (4). The nitrogen generated from this mechanism proceeds to form NO through Eq. (2) and Eq. (3).

$$CH + N_2 \leftrightarrow HCN + N, \quad (4)$$

NO production through N_2O route occurs through the free body recombination reactions, Eq. (5), under the conditions of high pressures.

$$N_2 + O + M \leftrightarrow N_2O + M, \quad (5)$$

where M is an energy carrier. The N_2O formed in Eq. (5) reacts with O to form NO through Eq. (6).

$$N_2O + O \leftrightarrow NO + NO, \quad (6)$$

Combustion of fuels that contain nitrogen results in formation of NO_x. Most fuels used in internal combustion engines contains contain very little or no Fuel Bound Nitrogen, as noted by DeCorso and Clark [18], and hence, Fuel NO_x is neglected in this work.

In Kioni *et al.* [19], kinetic modeling study of NO formation in methyl formate flames in freely propagating flames, homogenous system and counter-flow diffusion flames at low pressures, 1 bar, and equivalence ratio of 1 showed low NO formation in this fuel when compared to the case of methane/air and methanol/air in all the three flow configurations. This is not in agreement with prior experimental investigations by Rao [20] and Gerhard *et al.* [21] that have reported high NO formation in biodiesel. In this work, the effect of pressure (p) on the formation of NO in diffusion flames of CH_3OCHO is investigated. The results obtained are compared with those of methane and methanol under the same conditions. This is important because combustion in diesel engines occurs at high pressures, high temperatures and at various fuel-air equivalence ratios.

This paper is presented in four sections. Following this introduction is the modelling which covers the mathematical problem, the reaction equations and kinetics; and the solution method. Next is the results and discussion section which is followed by conclusions.

II. Numerical Modeling

The flow configuration considered is shown in Fig. 1. The fuel and air are positioned on the left and right hand side

respectively. The initial temperature of both fuel and air streams is taken as 300 K. The flames have been computed at constant pressures of 1 atm and 50 atm and at a strain rate of 30 s^{-1}. The computational domain for the three fuels is 12 mm. At the left hand side (fuel nozzle), pure fuel concentration (mole fraction of 1) is specified, while at the air nozzle, the mole fractions of O_2 and N_2 are specified as 21 % and 79 % respectively from the air-standard composition. The governing equations applied in this case are those for 2-D planar or axial-symmetric configuration. The dependent quantities of interest in this case are velocity components u and v, density ρ, pressure p, temperature T, mass fraction Y_i, i = 1, 2,…,N. These variables are governed by mass conservation equation, momentum equations, species conservation equation, the energy equation and the equation of state. The full set of simplified governing equations and the assumptions resulting to their simplifications are available in Kioni *et al.* [19].

A. Numerical Solution Method

The numerical solution method for the governing equations, and determination of transport and thermodynamics data is provided in Rogg [22]. The numerical solutions for the governing equations is implemented in RUN1Dl code in COSILAB software package [23].

B. Chemical Kinetics

The reaction mechanism for methane is the GRI-3.0 reaction mechanism, Smith *et al.* [24], which is then modified and extended using additional reactions given in Curran [13] and Petersen *et al.* [11] so as to cover the methane oxidation at high pressures. The latter additional reaction equations are presented in Table I. Methanol flames are computed using a comprehensive mechanism by Held and Dryer [16] combined with Leeds NO_x oxidation mechanism. The mechanism has also been modified and extended with high pressure rate coefficients reported by Sheng *et al.* [17], and herein given in Table 2. Finally, methyl formate flames reaction mechanism is that reported by the Dooley *et al.* [6] combined with the Leeds NO_x mechanism. It is further modified with QRRK high pressure rate parameters for the major decomposition channel, CH_3OCHO CH_3OH+CO as proposed by Dooley *et al.* [7]. This mechanism incorporates high pressure rate coefficients for methanol mechanism given in Table II.

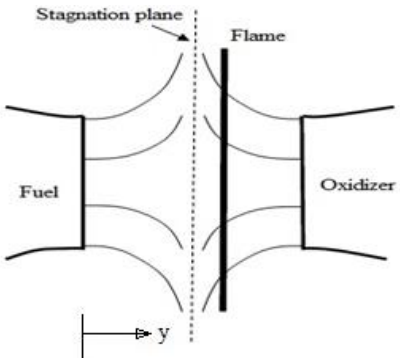


Fig. 1. Illustration of counter flow configuration for the study of a diffusion flame.

TABLE I: ADDITIONAL REACTIONS FOR METHANE SYSTEM AT HIGH-PRESSURES (HUNTER *ET AL*. 1994, PETERSEN *ET AL*. 1999)

Reaction	A	n	Activation Energy cal/mol
$CH_3O_2+H \leftrightharpoons CH_3O+OH$	9.6E+013	0.00	0.00
$CH_3O_2+O \leftrightharpoons CH_3O+O_2$	3.6E+013	0.00	0.00
$CH_3O_2+OH \leftrightharpoons CH_3OH+O_2$	6.0E+013	0.00	0.00
$CH_3O_2+HO_2 \leftrightharpoons CH_3O_2H+O_2$	4.6E+010	0.00	-2581.20
$CH_3O_2+HCO \leftrightharpoons CH_3O+H+CO_2$	3.0E+013	0.00	0.00
$CH_3O_2+CH_3 \leftrightharpoons CH_3O+CH_3O$	2.0E+013	0.00	0.00
$CH_3O_2+H_2O_2 \leftrightharpoons CH_3O_2H+HO_2$	2.4E+012	0.00	9942.40
$CH_3O_2+CH_2O \leftrightharpoons CH_3O_2H+HCO$	2.0E+012	0.00	11663.20
$CH_3O_2+CH_3O_2 \leftrightharpoons CH_3O+CH_3O+O_2$	7.8E+010	0.00	0.00
$CH_3O_2+CH_3O_2 \leftrightharpoons CH_3OH+CH_2O+O_2$	1.3E+011	0.00	0.00
$H_2O_2+M \leftrightharpoons OH+OH+M$	1.0E+017	0.00	45410.00
$H+H_2O_2 \leftrightharpoons HO_2+H_2$	1.7E+012	0.00	3752.30
$H+H_2O_2 \leftrightharpoons OH+H_2O$	1.0E+013	0.00	3585.00
$OH+H_2O_2 \leftrightharpoons HO_2+H_2O$	7.0E+012	0.00	1434.00
$O+H_2O_2 \leftrightharpoons OH+HO_2$	2.8E+013	0.00	6405.00
$O+HO_2 \leftrightharpoons OH+O_2$	2.0E+013	0.00	0.00
$H+HO_2 \leftrightharpoons O+H_2O$	5.0E+012	0.00	1410.10
$H+HO_2 \leftrightharpoons O_2+H_2$	2.5E+013	0.00	693.10
$H+HO_2 \leftrightharpoons OH+OH$	1.5E+014	0.00	1003.80
$OH+HO_2 \leftrightharpoons O_2+H_2O$	6.0E+013	0.00	0.00
$HO_2+HO_2 \leftrightharpoons O_2+H_2O_2$	4.2E+014	0.00	11973.90

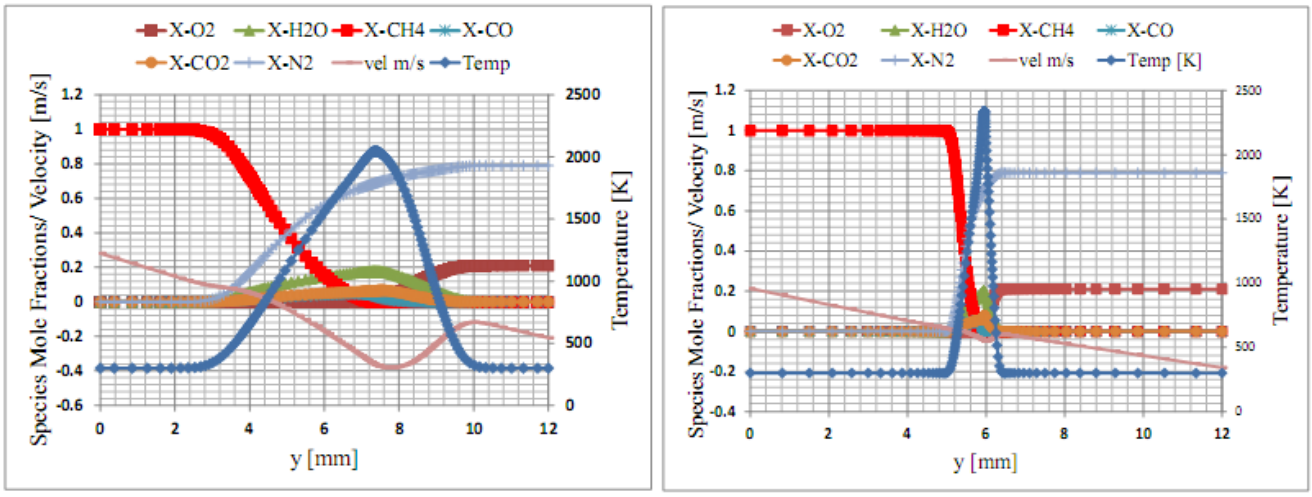
TABLE II: HIGH-PRESSURE LIMIT RATE COEFFICIENTS FOR THE CH3OH AND CH3OCHO (SHENG *ET AL*. 2002)

Reaction	A	n	Activation Energy (cal/mol)
$CH_3+OH \leftrightharpoons CH_3OH$	3.3133E06	2.07650	-1755.10
$CH_3OH \leftrightharpoons CH_3+OH$	3.2591E10	2.05451	90347.00
$CH_3OH \leftrightharpoons CH_2OH+H$	1.6369E07	2.54513	91951.00
$CH_3OH \leftrightharpoons CH_3O+H$	1.1908E07	2.38792	99614.00
$CH_3OH \leftrightharpoons CH_2O+H_2$	1.1004E09	1.28149	90233.00
$CH_3OH \leftrightharpoons HCOH+H_2$	2.0299E10	1.22342	86411.00
$CH_3OH \leftrightharpoons CH_2+H_2O$	2.8735E11	1.60030	92538.00

III. Results and Discussions

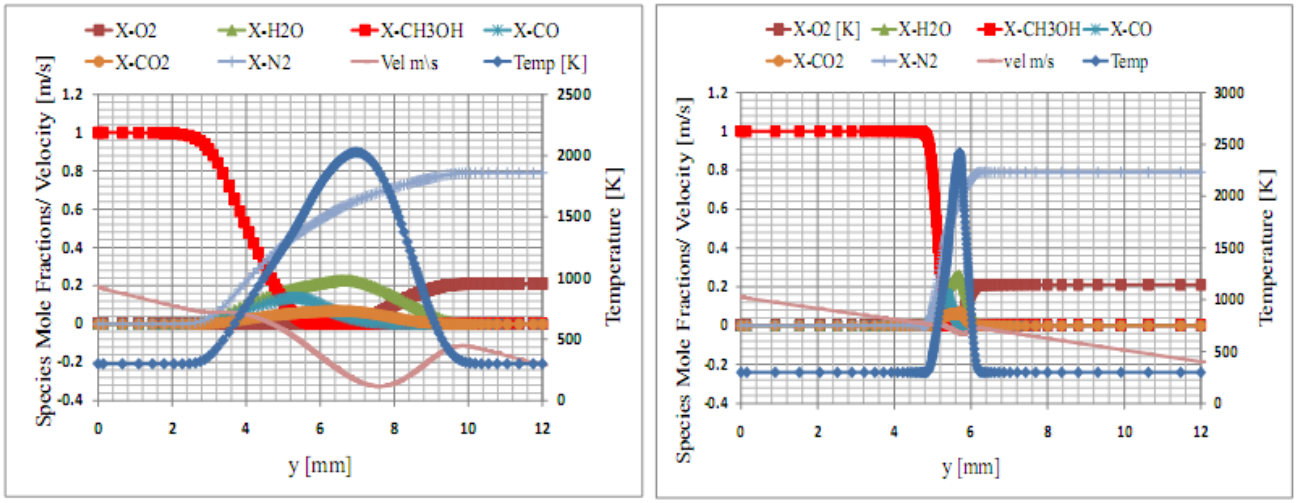
Fig. 2-Fig. 4, represents the structure of methane/air, methanol/air and methyl formate/air diffusion flames respectively at pressures of 1 atm and 50 atm. In a diffusion flame, the flame is established at the point where the mixture fraction is stoichiometric. For the case of 1 atm the stagnation plane is located at 4.6 mm, 4.8 mm and 5.2 mm respectively for methane, methanol and methyl formate flames. The figures depict that the flames are established at the air side (right hand side of the stagnation plane). For instance, at 1 atm pressure, methane, methanol and methyl formate flames are approximately at 2.8 mm, 2.4 mm and 1.8 mm respectively from the stagnation plane (the plane where the velocity, vel=0). When the pressure is increased to 50 atm, methane, methanol and methyl formate flames are approximately at 0.56 mm, 0.5 mm and 0.37 mm respectively from the stagnation plane. This, is expected because the stoichiometric mixture of these fuels requires more mole fractions of air than fuel. Thus, the fuel diffuses across the stagnation plane.

Fig. 2-Fig. 4 also show that increase in pressure decreases flame thickness. For example, at 1 atm, the thickness of methane, methanol and methyl formate flames are 6.8 mm, 7.5 mm and 7.0 mm respectively. While at 50 atm, the thickness of methane, methanol and methyl formate flames are approximately 3.6 mm, 2.4 mm and 1.6 mm respectively. This reduction in flame thickness is attributed to the high rate of heat release at high pressures (50 atm) that make the combustion reaction to take place within a very thin region. These findings are consistent with Heravi *et al.* [25] findings that showed that the thickness of the flame increases by increasing both temperature and pressure; however, pressure has the most effect on the flame thickness. In the three flames, the mole fractions of reactants, CH_4/O_2, CH_3OH/O_2 and CH_3OCHO/O_2 fall to near zero values at the axial location corresponding to the position of peak temperature, CO_2 and H_2O occurrence. It is interesting to note that higher concentration of CO is observed in CH_3OCHO flame compared to that of CH_3OH and CH_4 flame. This is because methyl formate mainly decomposes to form CH_3OH and CO. This is well illustrated in Fig. 4 that shows that peak concentrations of CH_3OH and CO in methyl formate flame occurs in the same axial location. The CO formed is then converted to CO_2 at this region due to presence of oxygen.



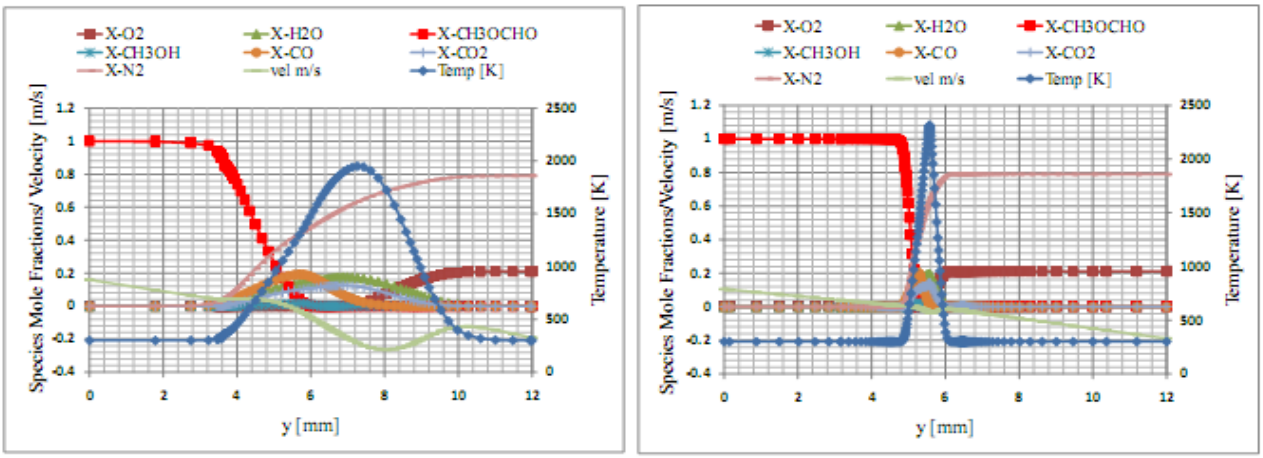
(a) 1 atm (b) 50atm

Fig. 2. Methane/air diffusion flame structure.



(a) 1 atm (b) 50 atm

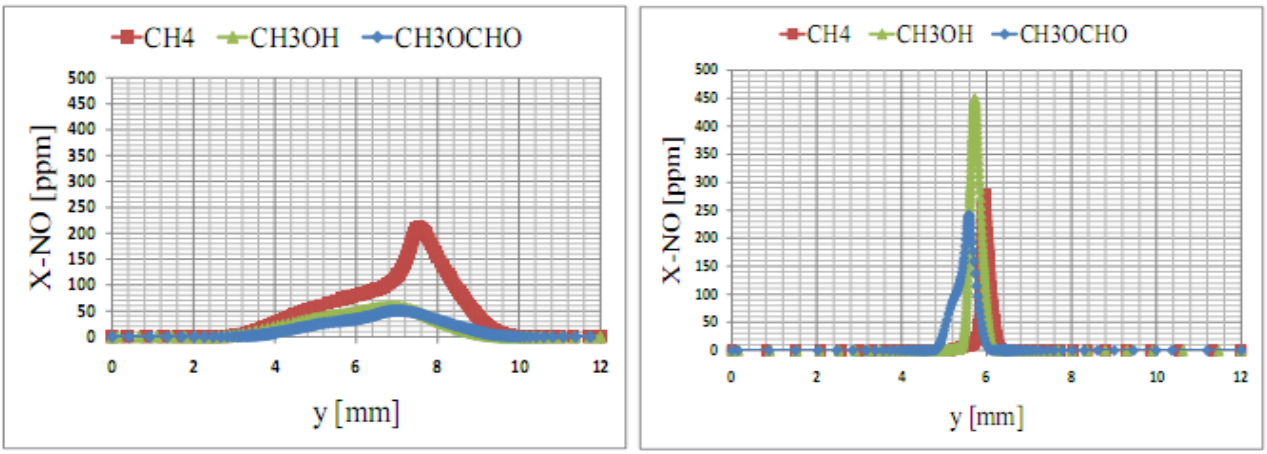
Fig. 3. Methanol/air diffusion flame.



(a) 1 atm (b) 50 atm

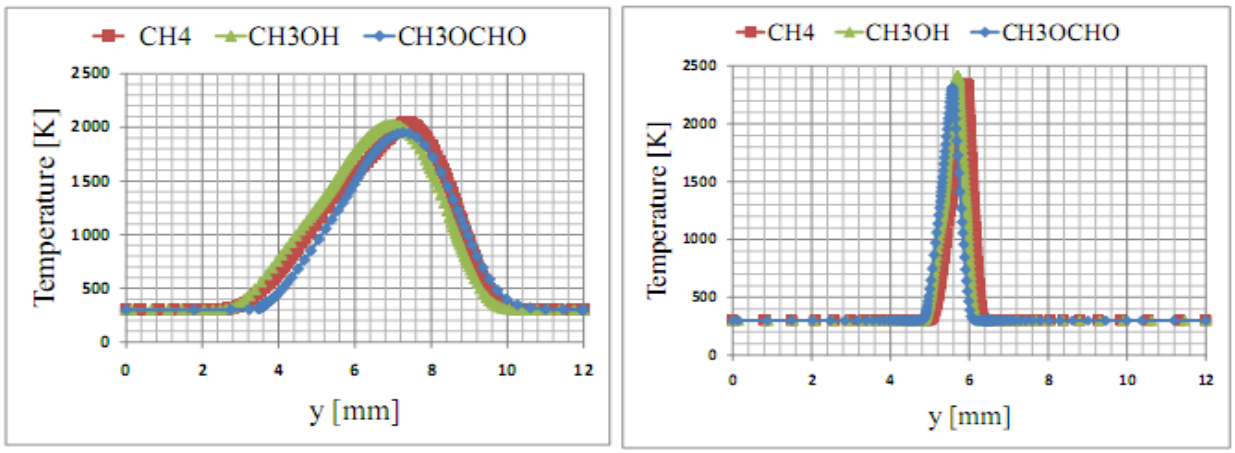
Fig. 4. Methyl formate/air diffusion flame.

Shown in Fig. 5-Fig. 14 are the species concentration profiles for NO and other species related to its formation. A comparison of NO formation in the three flames at 1 atm and 50 atm is shown in Fig. 5. The plot reveals that at 1 atm NO formation in higher in methane than in methanol and methyl formate flames respectively by 262 % and 315 %. However, when the pressure is increased to 50 atm, formation of NO becomes higher in methanol flame than in methane and methyl formate flame respectively by 60.5 % and 85.8 %. Fig. 5 also shows that NO formation has positive correlation to increase in pressure; for instance, an increase in pressure from 1 atm to 50 atm, results to 32.8 %, 672 % and 376 % increase in NO formation in methane, methanol and methyl formate flames respectively. This is expected because the high temperatures observed at high pressures (50 atm) increases thermo NO formation. The difference in NO formation in the three fuels at 1 and 50 atm is explained by looking at the temperature profiles and concentration profiles for the species responsible for NO formation.



(a) 1 atm (b) 50 atm

Fig. 5. NO concentrations in methane, methanol and Methyl formate.

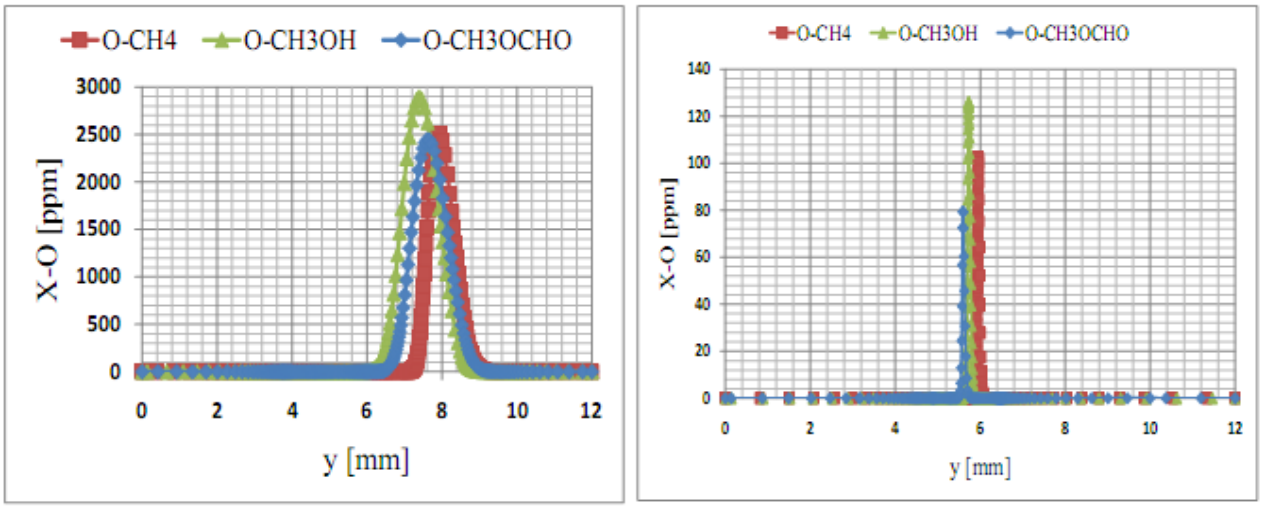


(a) 1 atm (b) 50 atm

Fig. 6. Temperature profiles for methane, methanol and Methyl formate.

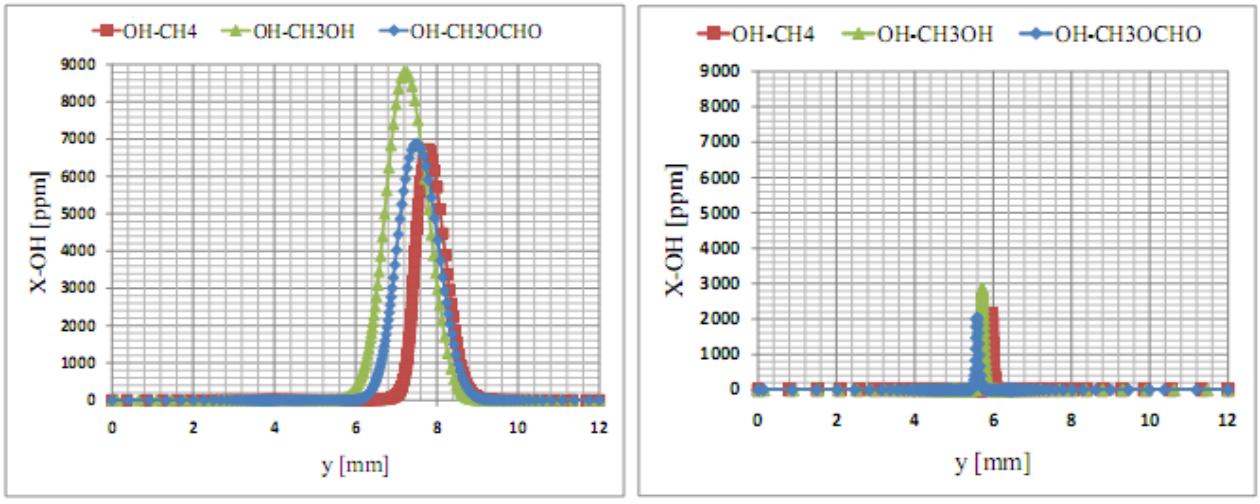
A comparison of temperature profiles for three fuels is shown in Fig. 6. The diagrams show that the temperature profiles for the three fuels have a similar shape. However, a slight variation on the peak temperature and the position of the peak temperature is observed. At 1 atm, methane, methanol and methyl formate flames attains peak temperatures of 2047 K, 2026 K and 1950 K respectively. However, when pressure is increased to 50 atm, higher peak temperature of 2415 K is observed in methanol flame compared to methane and methyl formate flames that has peak temperatures of 2336 K and 2314 K respectively. The observed increase in temperature with increase in pressure in the three fuels is expected since pressure is directly proportional to temperature as specified in the equation of state. At 50 atm, the flame thickness is very small as compared to flame thickness at low pressure (1 atm). This also explains the steep temperature gradient at 50 atm in methane, methanol and methyl formate flames.

A comparison of O and OH radicals for the three fuels is shown in Figs. 7 and 8. O and OH radicals play a significant role in both prompt-NO and thermo NO formation respectively through the reactions: N+OH→NO+H and N_2+O→NO+N. The plots show that more OH radicals are formed compared to O radicals at both 1 and 50 atm. Methanol has the highest concentration of O and OH radicals as compared to methane and methyl formate.



(a) 1 atm (b) 50 atm

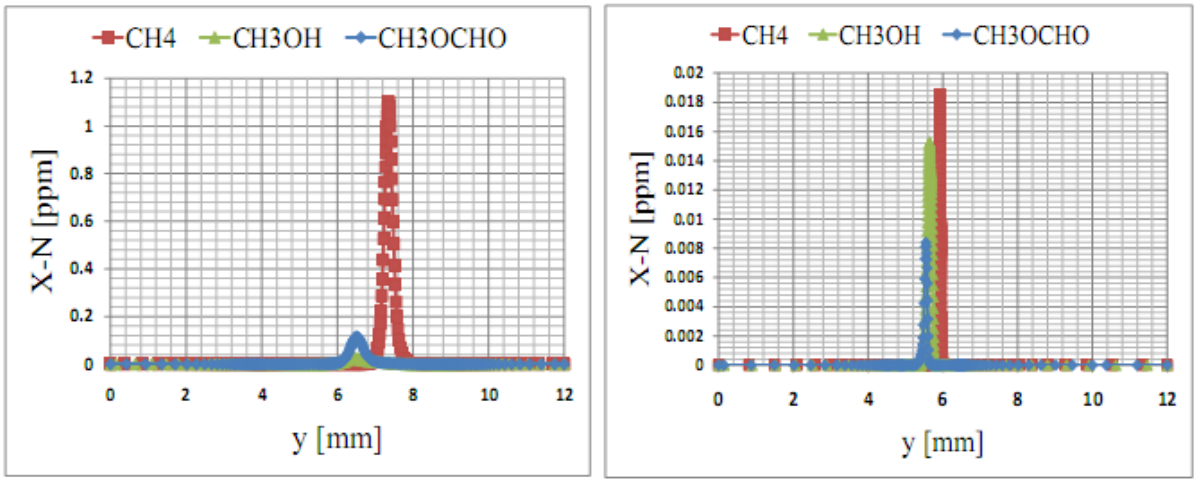
Fig. 7. O concentrations in methane, methanol and methyl formate.



(a) 1 atm (b) 50 atm

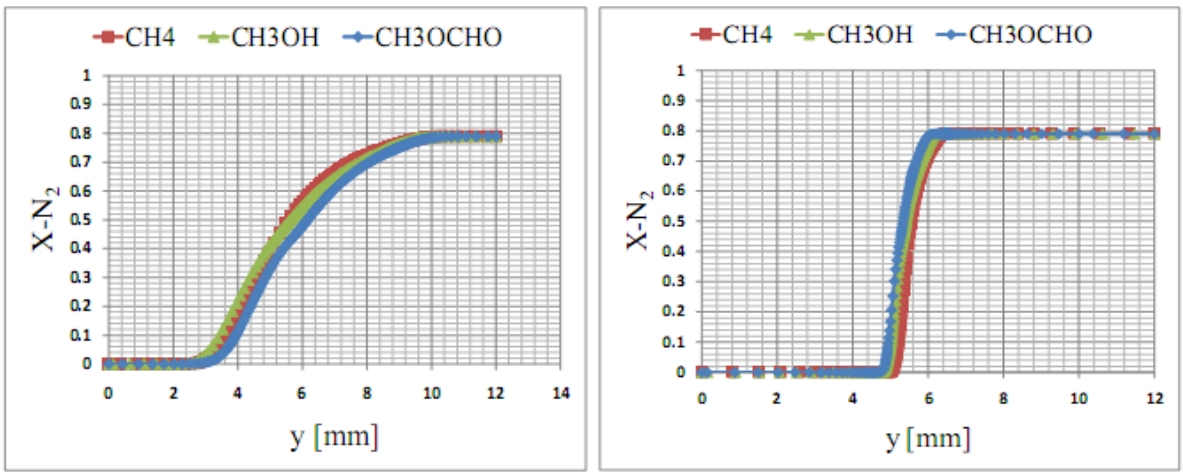
Fig. 8. OH concentrations in methane, methanol and methyl formate.

Fig. 10 compares N_2 mole fraction profiles at 1 atm and 50 atm. N_2 is an important species in the Zel'dovich reactionN_2+O→NO+N that results to the formation of NO and N. More NO is formed through this reaction because of high temperatures and the high concentration of O-radicals in the three fuels. Compared in Fig. 9 are the N radical's mole fraction profiles for the three fuels. N radical are mainly formed through the reactions N_2+O→NO+N and CH+N_2→HCN+N that are the initiation steps for thermo-NO and prompt-NO respectively. N radicals participate in NO formation through the reactions N+O_2→NO+O and N+OH→NO+H to form NO. This study, has shown that less than 10 ppm moles of N radicals are formed in the three flames at 1 and 50 atm. This implies that N radical has negligible contribution to the formation of NO in methane/air, methanol/air and methyl formate/air diffusion flames.



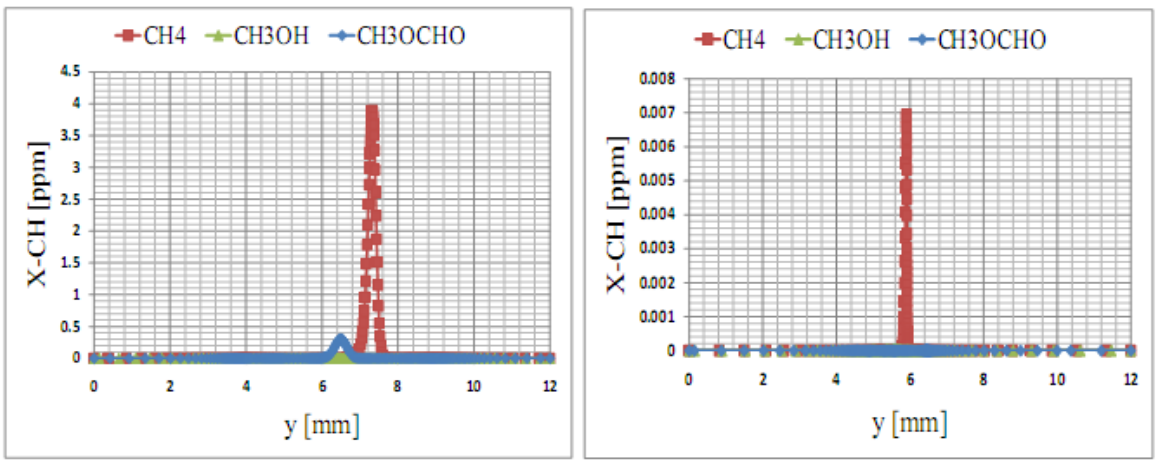
(a) 1 atm (b) 50 atm

Fig. 9. N concentrations in methane, methanol and methyl formate.



(a) 1 atm (b) 50 atm

Fig. 10. N_2 concentrations in methane, methanol and methyl formate.

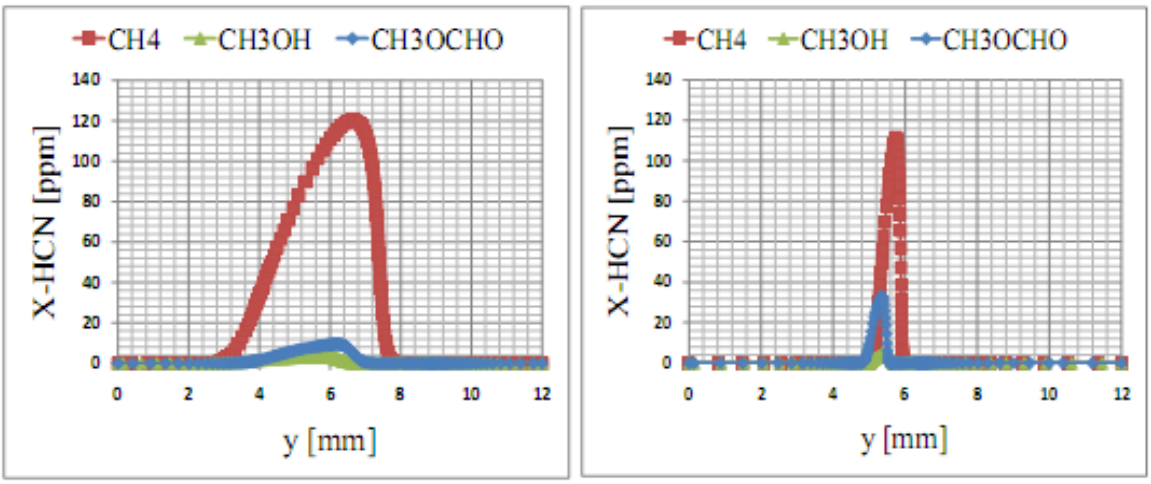


(a) 1 atm (b) 50 atm

Fig. 11. CH concentrations in methane, methanol and methyl formate.

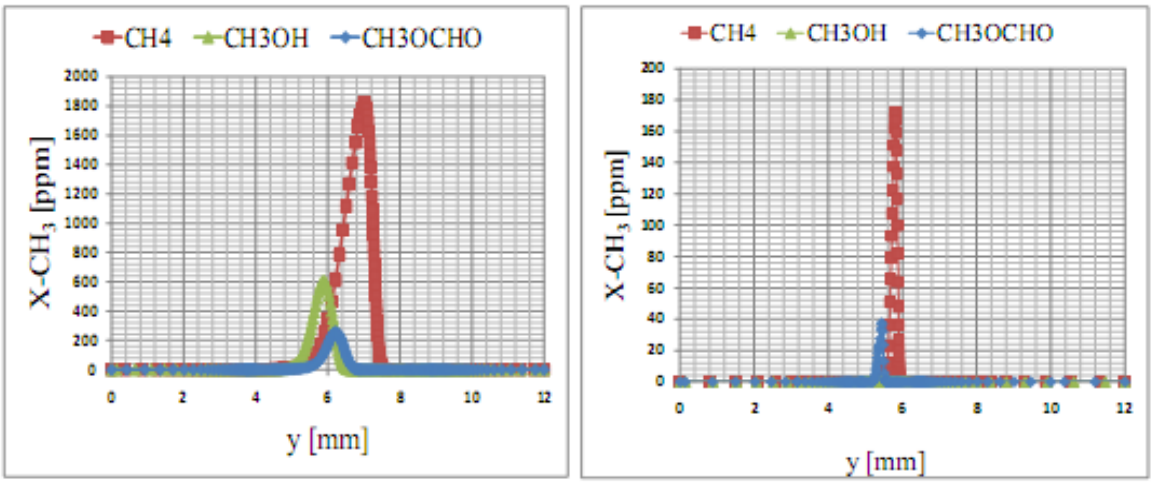
The formation of CH radicals in the three fuels is compared in Fig. 11. The moles of CH produced in the three fuels are less than 5 ppm and this explains the low concentration of N radicals in the three fuels. Comparison of HCN radicals in Fig. 12 show high HCN formation in methane flame as compared to methanol and methyl formate flame. The high concentration of HCN in methane flame is attributed to the reaction $CH_3+N \rightarrow HCN+H_2$ because of the high concentration of CH_3 radicals as shown in Fig. 13. N_2O concentration profile comparison is presented in Fig. 14. The plot shows low (less than 3 PPM) N_2O formation in CH_4, CH_3OH and CH_3OCHO flames at 1 and 50 atm. This implies that the effect of N_2O to the formation of NO in the three fuels is negligible. The low concentration of N, CH and N_2O observed in the three fuels implies that NO is mainly formed through the reaction, $N_2+O \rightarrow NO+N$. The high NO formed in

CH_4 and CH_3OH at 1 and 50 atm respectively is thus attributed to this reaction because of high temperatures and high concentration of N_2 and O in these flames.



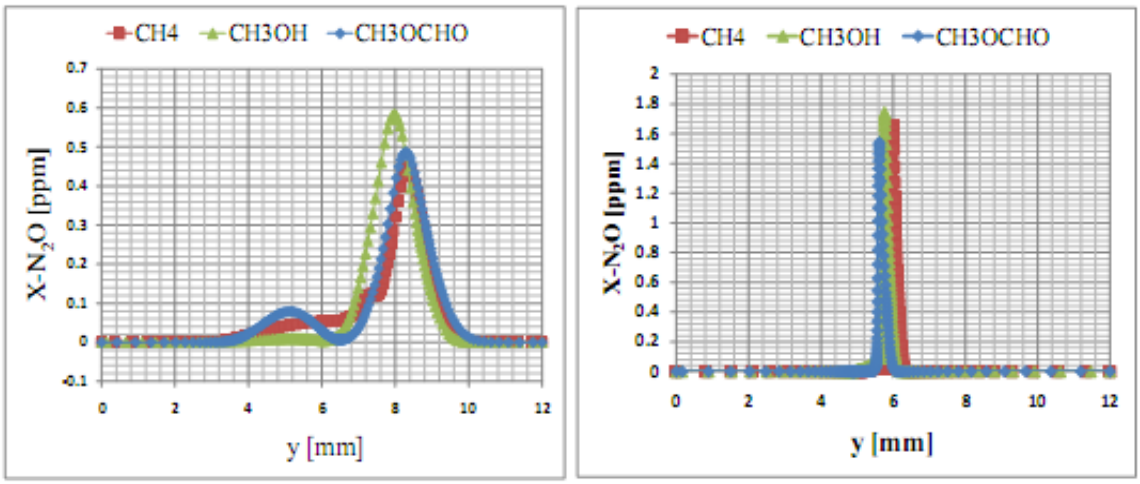
(a) 1 atm (b) 50 atm

Fig. 12. HCN concentrations in methane, methanol and methyl formate.



(a) 1 atm (b) 50 atm

Fig. 13. CH3 concentrations in methane, methanol and methyl formate.



(a) 1 atm (b) 50 atm

Fig. 14. N_2O concentrations in methane, methanol and methyl formate.

IV. Conclusions

It has been shown that pressure affects the structure of flames and formation of various species including oxides of nitrogen in diffusion combustion of CH_4, CH_3OH and CH_3OCHO. It has been established that, increase in pressure

results to reduction in flame thickness. This work attributes this observation to the high rate of heat release at high pressures (50 atm) that make the combustion reaction to take place within a very thin region. From this research, it has also been shown that in diffusion flames NO formation increases with increase in pressure. At 1 atm, high NO formation is observed in methane while at 50 atm NO formation is high in methanol. A comparison of N, HCN, N_2O, CH, O, OH and N_2 has shown that NO formation in diffusion flame mainly occurs through the reaction $N_2 + O \rightarrow NO + N$. This is because of the high concentration of O and N_2 observed in the three fuels. The results agree with the experimental observations of high NO_x emissions in engines utilizing the oxygenated biodiesel fuels than those operating on fossil based fuels. In this work, methyl formate (CH_3OCHO), the simplest methyl ester has been used to represent biodiesel. Thus, future research work should focus on using a surrogate fuel with high molecular mass and long chain length such as methyl butanoate and methyl deaconate in order to investigate the effect of molecular structure and carbon chain length on the formation of NO in ester fuels.

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REFERENCES

[1] S. A. Basha, K. R. Gopal, "A review on biodiesel production, combustion, emissions and performance," *International Journal of Applied Environmental Sciences*, vol. 5, pp. 23–30, 2008.

[2] H. P. Liu, S. S. Strank, W. Mike, R. Hebner, and J. Osara, "Combustion and emission modelling and testing of neat biodiesel fuel," in *Proc. the ASME 2010 4th International Conference on Energy Sustainability*, 2010.

[3] S. Ekarong, "Synergistic effects of alcohol-based renewable fuels: fuel properties and emissions," Ph.D. thesis, University of Birmingham, 2013.

[4] S. G. Michael, L. M. Robert, L. A. Teresa, M. H. Andrew, "Effect of biodiesel composition on NO_x and pm emissions from a ddc series 60 engine," Tech. Rep., National Renewable Energy Laboratory, 1999.

[5] L. Magin, A. Octavio, R. Jose, "Effect of biodiesel fuels on diesel engine emissions," *Progress in Energy and Combustion Science*, vol. 34, pp. 198–223, 2008.

[6] S. Dooley, F. L. Dryer, B. Yang, J. Wang, T. A. Cool, T. Kasper, N. Hansen, "An experimental and kinetic modelling study of methyl formate low-pressure flames," *Combustion and Flame*, vol. 158, pp. 732–741, 2011.

[7] S. Dooley, M. P. Burke, M. Chaos, Y. Stein, F. L. Dryer, V. P. Zhukov, O. Finch, J. M. Simmie, H. J. Curran, "Methyl formate oxidation: speciation data, laminar burning velocities, ignition delay times, and a validated chemical kinetic model," *International Journal of Chemical Kinetics*, vol. 42, pp. 527–549, 2010.

[8] J. S. Francisco, "Mechanistic study of gas-phase decomposition of methyl formate," *Journal of the American Chemical Society*, vol. 125, pp. 10475–10480, 2003.

[9] W. K. Metcalfe, J. M. Simmie, and H. J. Curran, "Ab initio chemical kinetics of methyl formate decomposition: The simplest model biodiesel," *Journal of Physics and Chemistry*, vol. 114, pp. 5478–5484, 2010.

[10] T. B. Hunter, B. H. Wang, T. A. Litzinger, and M. Frenklach, "The oxidation of methane at elevated pressures: Experiments and modeling," *Combustion and Flame*, vol. 97, pp. 201–224, 1994.

[11] E. L. Petersen, D. F. Davidson, and R. K. Hanson, "Kinetics modeling of shock-induced ignition in low-dilution CH_4/O_2 mixtures at high pressures and intermediate temperatures," *Combustion and Flame*, vol. 117, pp. 272–290, 1999.

[12] S. Sibendu and K. A. Suresh, "A numerical investigation of methane air partially premixed flames at elevated pressures," *Combustion Science and Technology*, vol. 179, no. 6, pp. 1085–1112, 2007.

[13] H. J. Curran, "Detailed chemical kinetic modelling: Is there life after GRI-MECH 3.0," *Fuel Chem*., vol. 49, no. 1, pp. 263–264, 2004.

[14] D. D. Thomsen, F. F. Kuligowski, and N. M. Laurendeau, "Modeling of NO formation in premixed, high-pressure methane Flames," *Combustion and Flame*, vol. 119, pp. 307–318, 1999.

[15] G. Rozenchan, D. L. Zhu, C. K. Law, and S. D. Tse, "Outward propagation, burning velocities, and chemical effects of methane flames up to 60 atm," in *Proc. Combust. Inst.*, 2002, pp. 1461–1469.

[16] T. J. Held and F. L. Dryer, "A comprehensive mechanism for oxidation of methanol," *Chemical Kinetics*, vol. 30, pp. 805–830, 1998.

[17] C. Sheng, J. W. Bozzelli, and I. Wen-chiun, "Development of a pressure dependent reaction model for methane/methanol mixtures under pyrolytic and oxidative conditions and comparison with experiment," Fuel Chemistry Division, New Jersey Institute of Technology, Newark, vol. 47, no. 1, pp. 98–102, 2002.

[18] S. M. DeCorso and J. S. Clark, *Stationary Gas Turbine Alternative Fuels*, ASTM International, 1983.

[19] P. N. Kioni, J. K. Tanui, and A. Gitahi, "Numerical simulations of nitric oxide (NO) formation in methane, methanol and methyl formate in different flow configurations," *Journal of Clean Energy Technologies*, vol. 1, pp. 151–156, 2013.

[20] P. V. Rao, "Effect of properties of karanja methyl ester on combustion and NO_x emissions of a diesel engine," *Journal of Petroleum Technology and Alternative Fuels*, vol. 2, pp. 63–75, 2011.

[21] K. Gerhard, C. A. Sharp, and T. W. Ryan, "Exhaust emissions of biodiesel, petroldiesel, neat methyl esters, and alkanes in a new technology engine," Energy and Fuel, vol. 20, pp. 403–408, 2006.

[22] B. Rogg, "Adaptive methods in computational fluid dynamics of chemically reacting flows," *Numerical Methods in Engineering*, vol. 90, pp. 659–670, 1991.

[23] COSILAB Version 3. (2009). Rotexo-Cosilab GmbH & Co. KG, Bad Zwischenahn, Germany. [Online]. Available: www.rotexo.com

[24] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner Jr., and Z. Lissianski. Gri 3.0 mechanism. [Online]. Available: http: //www.me.berkeley.edu/gri − mech

[25] H. Heravi, A. Azarinfar, S. Kwon, P. Bowen, and N. Syred, "Determination of laminar flame thickness and burning velocity of methane-air mixture," in *Proc. Third European Combustion Meeting*, 2007.

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