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Final Report

METRANS Research Project 08-01: Combustion and Emission Characteristics of Biofuels Used for Transportation

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Abstract

The world faces both an energy crisis and the problem of global warming due to increasing emissions of green-house gases, particularly CO_2 . Because of dwindling petroleum reserves in the USA, there is an urgent need to develop alternative fuels. Bioderived fuels are one of the most viable and affordable alternatives. We focus on several biofuels, specifically dimethyl-ether (DME), a clean fuel derived through processing of biomass-derived syngas, and several low molecular weight methyl-esters as surrogates of fatty acid methyl-ester (FAME) type biofuels. We study the fundamental combustion characteristics of these fuels and their pollutant emissions, particularly nitrogen oxides (NO_x).

We provide insight into the combustion characteristics of DME and its high temperature kinetics. We measure laminar flame speeds and extinction limits of DME/air mixtures using the counterflow configuration and compare them to published experimental data and to numerical simulations using an updated kinetic model. Sensitivity and reaction pathway analyses provide insight into the controlling physico-chemical processes. The laminar flame speeds and extinction limits of two C₄ (methyl butanoate (MB) and methyl crotonate (MC)), and one C₁₀ (methyl decanoate (MD)) FAME were measured and analyzed. The NO_x emissions of MB, MC, and MD were measured, simulated, and compared with those of n-pentane, *n*-decane and *n*-dodecane. These studies gave a better understanding of the processes that lead to NO_x formation and means to minimize such emissions during the use of biofuels. Project data and simulations are a key step towards meeting the long-term goal of the development and testing of surrogates and the attendant detailed kinetic mechanism of methyl-stearate, a FAME with a straight chain saturated hydrocarbon section with 18 carbon atoms, typically found in common biodiesel fuels.

1. Introduction

The world currently faces the simultaneous threats of a potentially crippling energy crisis and the emerging environmental problem of global warming due to increasing emissions of green-house gases, particularly CO₂. Due to the instability of world politics, the surging global demand for petroleum along with dwindling petroleum reserves in the USA, there is an urgent need today for the nation to develop alternative fuels. Implementing the use of bioderived fuels is one of the most viable and affordable solutions for reducing our dependence on conventional petroleum. The use of biofuels, furthermore, promises to reduce greenhouse gas emissions, thus lessening the threat of global warming. In this study, we have focused our attention on a number of model biofuels specifically dimethyl-ether (DME), a very promising clean fuel that can be derived through processing of biomass-derived syngas, and several low MW methyl-esters as surrogates of fatty acid methyl-ester (FAME) type biofuels. We have studied the fundamental combustion characteristics of such fuels, as well their pollutant emissions, particularly nitrogen oxides (NO_x), as it is important that the use of such fuels, though beneficial in some respects (reduction of greenhouse gas emissions), does not result in an increase of other emissions. This Final Report provides a brief description of the work that we have carried out as part of our METRANS supported project. In the report we first provide background information on the various fuels we have investigated; we then describe the experimental and numerical methodology we have followed during our study, followed by a brief overview of our key technical findings. We conclude with the description of future work which is supported by grants from NASA and DOE which were secured using the METRANS support as seed-funding.

1.1 Background

1.1.1 Dimethyl-Ether

Dimethyl-ether, or CH₃OCH₃, has garnered considerable attention recently as one of the most promising and suitable alternative fuels. DME is the simplest of all ethers, with physical properties similar to LP Gas, boiling at -25 °C at atmospheric pressure, and condensing at 6 bar and 25 °C. It is currently manufactured mostly from natural gas or coal, but it can also be conveniently produced from biomass-derived syngas [[1], [2]]. It can be

used for stationary power generation (e.g., turbines and IC engines), as a transportation fuel in diesel engines, and also as a hydrogen carrier for mobile applications involving PEM fuel cells.

Extensive studies on DME performance in diesel engines have already been carried out [[3]-[5]]. It has been shown that DME is a desirable fuel due to its high Cetane number (> 55) and volatility that give rise to short ignition delays, low noise levels, and good cold-start characteristics. DME has been shown to result in reduced NO_x, HC, and CO emissions, and not to produce soot. HCCI combustion of DME has been investigated both experimentally and numerically [[6]-[8]]. Experiments have shown that stable HCCI operation can be obtained over a quite broad range of engine speeds and loads using a DME/methanol fuel blend [6]. Promising results for adjusting ignition timing and heat release through the use of additives such as methanol, ozone [7], and formaldehyde [8] have been obtained.

Curran and coworkers have developed a detailed DME kinetic mechanism [9] using a combination of experimental data of DME oxidation in a jet stirred reactor [10] at 1 and 10 atm and a temperature range of $800 \sim 1300$ K, and ignition delay times obtained behind reflected shock waves [11] at 13 and 40 bar, and a temperature range of $650 \sim 1300$ K. The mechanism has been subsequently updated [12] to fit jet stirred reactor data at 10 atm in the lower temperature range of $550 \sim 800$ K. Fisher *et al.* [[13], [14]] further investigated the pyrolysis and oxidation of DME both in an atmospheric and in a variable-pressure flow reactor. High-temperature pyrolysis [13] was studied at 2.5 atm and 1060 K, and high-temperature oxidation at atmospheric pressure and at 1118 K [13]. Furthermore, the low-temperature oxidation was investigated over reactor temperature and pressure ranges of $550 \sim 850$ K and $12 \sim 18$ atm respectively [14]. These studies have shown that DME exhibits NTC behavior, and that formic acid is a major intermediate of the low temperature oxidation. Consequently, a revised mechanism was proposed which also includes the chemistry leading to formic acid formation. Simulations reproduced the experimental results very satisfactorily.

Kaiser *et al.* [15] determined the species profiles of two DME/air flat flames, with equivalence ratios of $\phi = 0.67$ and 1.49, both experimentally and numerically using the mechanism of Fischer *et al.* [13]. Results showed that CH₂O mole fractions were 5–10 times

larger in DME flames compared to methane flames of similar ϕ . Predicted species profiles were in reasonable agreement with experimental results, except for the lean DME flame, for which hydrocarbon species, other than CH₂O, were over-predicted by a factor of 3. McIlroy *et al.* [16] used the mechanism of Curran *et al.* [9] to predict the species profiles of lowpressure burner-stabilized flames of DME/O₂/Ar mixtures at 30 Torr for $\phi = 0.98$ and 1.20. Good agreement was found, in general, between experiments and predictions for all species profiles, with the exception of CH₃. More recently, Brackmann *et al.* [17] performed quantitative measurements of temperature and species concentrations in a DME-air counterflow diffusion flame.

Daly *et al.* [18] measured laminar flame speeds, S_u^o , of DME/air mixtures using a constant-volume spherical bomb. The experimental results were modeled using an updated mechanism [15] that had only minor differences from that reported by Fischer *et al.* [13], and notable differences were found. The rate constants of the following three formyl-radical decomposition reactions were modified by factors of $\frac{1}{2}$, 3, and 3 respectively

 $HCO + M \rightarrow H + CO + M$ $HCO + OH \rightarrow CO + H_2O$ $HCO + CH_3 \rightarrow CH_4 + CO$

in order to bring the computed $S_u^{o's}$'s into agreement with their measurements. Zhao *et al.* [19] measured $S_u^{o's}$'s using the stagnation flame burner configuration with digital particle image velocimetry (DPIV), and reported values significantly higher to those by Daly *et al.* [18] for all ϕ 's. In the same study, the experimental results were simulated using the mechanism of Fischer *et al.* [13], and close agreements were found. Qin *et al.* [20] measured $S_u^{o's}$'s in a spherical bomb at pressures up to 10 atm. At atmospheric pressure, the $S_u^{o's}$'s of Qin *et al.* [20] were in good agreement with those of Daly *et al.* [18] on the lean side, but higher on the rich side. However, they were considerably lower than those of Zhao *et al.* [19] for all ϕ 's. Results also showed that the $S_u^{o's}$'s of DME/air mixtures decrease considerably as pressure increases. $S_u^{o's}$'s of CH₄/air mixtures were computed, using the Fischer *et al.* [13], with the three formyl decomposition reaction rates modified

as proposed in [18]. This resulted in a peak S_u^o of 28.8 cm/s, which is too low, and the peak position shifted to the lean side, thus proving that the DME mechanism cannot be corrected by simply adjusting the three formyl decomposition reaction rates. Jomaas [21] determined S_u^o 's for DME/air/He mixtures in a constant pressure chamber at pressures up to 20 atm. Results were in close agreement with those reported by Qin *et al.* [20] at all pressures.

Zheng *et al.* [22] studied the ignition of nitrogen-diluted DME by counterflowing heated air at pressures from 1.5 to 3 atm. Simulations using the Curran *et al.* mechanism [9] overpredicted the ignition temperatures, while an updated mechanism [23] produced close agreement with all experimental data. Chen *et al.* [24] studied the effect of DME addition on the high temperature ignition and propagation of CH_4/air mixtures. Numerical results showed that the addition of DME has a dramatic ignition enhancement.

The main goal of our study was to provide further insight into the combustion characteristics of DME and its high temperature kinetics by resolving a number of issues that still remain unresolved pertaining to both the experiments as well as the modeling of DME flames. Laminar flame speeds and extinction limits of DME/air mixtures were measured using the counterflow configuration. These measurements were compared to published experimental data and to numerical simulations using an updated kinetic model. Sensitivity and reaction pathway analyses were conducted in order to provide insight into the controlling physico-chemical processes.

1.1.2 Methyl-Esters

Fatty acid methyl-esters are the primary components of biodiesel, which are made from renewable resources such as vegetable oil or animal fat through the transesterification process. This process, involve reaction of the base oil with an alcohol (typically ethanol or methanol) over a catalyst (typically sodium or potassium hydroxide) in order to convert the oil into a mixture of mono-alkyl esters of long chain fatty acids in the C_{12} and C_{22} carbon range, with glycerin being the byproduct of this reaction.

The FAME-type biodiesel can be used in its pure form or can be blended with conventional diesel. It has a higher Cetane number, but a slightly lower energy content than typical petroleum-derived diesel fuels. It is biodegradable, non-toxic and contains no sulfur, so that sulfur oxide emissions are essentially eliminated. Due to its oxygen content, biodiesel use promises to significantly reduce unburned hydrocarbon, carbon monoxide, and particulate matter emissions. Since it is biomass-derived, it also reduces carbon dioxide emissions. On the other hand, oxygenated fuels are known to be associated with increased emissions of nitrogen oxide.

The effect of using biodiesel and biodiesel blends on particulate matter (PM) and nitrogen oxides (NO_x) emissions in Diesel engines has been studied by a number of investigators (e.g., [25]-[40]). These studies reveal a significant reduction in PM emissions, but at the expense of increased NO_x emissions. The chain length and the degree of saturation of fatty acid mono-alkyl esters have distinct effects on emissions [[33]-[35]]. NO_x emissions have been found to increase with increasing fuel density as well as the number of double bonds. For fully saturated fatty acid chains, NO_x emissions increase with decreasing chain length. Different strategies for reducing NO_x emissions have been considered by a number of investigators [[36]-[40]]. However, the substantial increase in NO_x emissions remains a potential hurdle for significant increase in biodiesel use.

Despite their use as practical fuels, the combustion characteristics of biodiesels are not yet well characterized and understood. Therefore, it is essential to advance the fundamental understanding of biodiesel combustion and evaluate the consequences of using them on engine performance and the environment. Achieving such understanding in well-controlled environments will allow for distinguishing the roles that the physical and chemical properties of biofuels play in determining the behavior that is observed and measured in engines.

At present, fundamental data and chemical kinetic models for actual biodiesels are not available. However, studies on lower molecular weight alkyl esters that act as candidate surrogates for complex biodiesels have appeared in the literature. Fisher *et al.* [41], for example, published a kinetic mechanism for methyl-butanoate (MB) with a smaller *n*-propyl (n-C₃H₇) group to simulate the C₁₆-C₁₈ portion of the usual biodiesel molecule. MB is a candidate biodiesel surrogate, as it has the essential structure characteristic of biodiesel fuels and the chemical features of larger methyl-esters. The mechanism was developed using experimental data of low-temperature oxidation in small, constant-volume, isothermal static reactors in the temperature range of 520 ~ 740 K and the pressure range of 13 ~ 54 kPa.

More recently, Gail *et al.* [42] updated the earlier mechanism by adding a C_4 sub-mechanism and modifying the rate constant parameters of the following three reactions:

$$CH_{3}CH_{2}CH_{2}(C=O)OCH_{3} + H \Rightarrow H_{2} + CH_{3}CH_{2}CH(C=O)OCH_{3}$$
$$CH_{3}O + M \Rightarrow CH_{2}O + H + M$$
$$C_{2}H_{3} + O_{2} \Rightarrow CH_{2}O + HCO$$

This modified mechanism was used to simulate experimental results obtained from three methods: a jet stirred reactor at atmospheric pressure in the temperature range of 800 - 1350 K, an opposed-flow diffusion flame at atmospheric pressure, and the Princeton variable pressure flow reactor at 1.266 MPa in the temperature range of 500 - 900 K. Simulations were in good agreement with experimental results except that the low reactivity in the jet stirred reactor between 850 and 1050 K was not predicted.

Huynh *et al.* [43] reported on a detailed kinetic mechanism for MB assembled using theoretical approaches. Several decomposition, isomerization, and propagation steps were determined using *ab initio* calculations. The new kinetic model was combined with the Fischer *et al.* [41] mechanism, and used to study the CO_2 formation during the pyrolysis of MB as well as to predict ignition delay times in a shock tube at different temperatures and pressures. The computed results agreed very well with literature experimental data.

More recently, a detailed chemical kinetic mechanism has been developed by Herbinet *et al.* [44] and used to study the oxidation of methyl-decanoate (MD), a more realistic surrogate for biodiesel fuels. Computed results have been compared with MD experiments in an engine and oxidation of rapeseed oil methyl esters in a jet-stirred reactor. This mechanism includes the ability to reproduce the unique early CO_2 formation due to the presence of the ester group in the reactant. These model capabilities indicate that large *n*-alkanes can be good surrogates for large *methyl*-esters and biodiesel fuels to predict overall reactivity, but more subtle kinetic details, including early CO_2 formation, can be predicted only by a detailed kinetic mechanism for a true *methyl*-ester fuel.

Hayes *et al.* [45] quantified the previously proposed CO_2 production pathway [44] using composite (G3B3) calculations and identified areas for potential side reactions, in both MB and methyl-pentanoate (MP). Alternative radical isomerizations were also examined and

suggest that side reactions may become increasingly competitive in the chemistry of longchain methyl-esters, compared to MB.

Westbrook *et al.* [46] have developed a detailed chemical kinetic reaction mechanism for a group of four small alkyl-ester fuels, consisting of methyl-formate, methyl-acetate, ethylformate, and ethyl-acetate. The mechanism was validated by comparisons between computed results and measured intermediate species mole fractions in fuel-rich, lowpressure, premixed laminar flames. The model development employs the principle of similarity of functional groups in constraining the H-atom abstraction and unimolecular decomposition reactions. The reaction mechanism and formalism for mechanism development are suitable for extension to biodiesel fuels.

Sarathy *et al.* [47] examined the combustion chemistry of a saturated (MB) and an unsaturated (methyl-crotonate (MC)) methyl-ester in opposed-jet diffusion flames and in a jet stirred reactor at atmospheric pressure. The results showed that both fuels have the same reactivity and that the MC combustion produces much higher levels of C_2H_2 , $1-C_3H_4$, $1-C_4H_8$ and $1,3-C_4H_6$ than MB, while MB exhibits higher levels of C_2H_4 . Compared to MB, MC was determined to produce more soot precursors such as benzene.

Dooley *et al.* [48] have studied the auto-ignition of MB at 1 and 4 atm in a shock tube over the temperature range 1250–1760 K. These measurements were complemented by auto-ignition data obtained in a rapid compression machine over the temperature range 640–949 K at compressed gas pressures of 10, 20, and 40 atm. The auto-ignition of MB was observed to follow Arrhenius-like temperature dependence over all conditions studied. Results showed that MB does not exhibit NTC behavior, as it has been reported for long-chain methyl esters [32].

Farooq *et al.* [49] studied the high-temperature decomposition of three simple methylesters, namely methyl-acetate, methyl-propionate, and MB behind reflected shock waves. CO_2 yield measurements were made over the range of temperatures 1260 - 1653 K and pressures of 1.4 - 1.7 atm. Model predictions using the Fisher *et al.* [41] mechanism for CO_2 yields during MB pyrolysis are significantly lower than those measured. However, an improved MB model [42] was found to provide substantially improved predictions.

Gail *et al.* [50] obtained new experimental results for the oxidation of MB and MC in a jet-stirred reactor at atmospheric pressure over the temperature range 850 - 1400 K.

Experimental data and modeling results showed that MC has reaction pathways analogous to that of MB. Key reaction pathways leading to the unsaturated ester forming higher levels of soot precursors and unsaturated hydrocarbons have been identified.

A jet-stirred reactor study of ethyl-propanoate, another model biodiesel molecule, has been carried out by Metcalfe *et al.* [51] at 10 atm pressure and for the temperature range of 750 - 1100 K. The experimental results were used to modify the rate constant of the six-centered unimolecular elimination reaction that produces ethylene and propanoic acid. The revised mechanism was then used to re-simulate shock tube ignition delay data with good agreement observed.

Walton *et al.* [52] studied the ignition of MB and *ethyl*-propanoate in a rapid compression facility. The effect of functional group size on ignition delay time was investigated using pressure time-histories and high-speed digital imaging. Results confirmed that MB consumption is dominated by relatively slow bimolecular H-atom abstraction reactions, whereas ethyl-propanoate consumption is dominated by faster unimolecular decomposition. A new mechanism for methyl-butanoate and ethyl-propanoate ignition was presented. HadjAli *et al.* [53] also studied the auto-ignition of a series of C₄ to C₈ methyl-esters in a rapid compression machine in the low and intermediate temperature region (650 - 850 K) and at higher pressures (4 - 20 bar). The oxidation scheme and overall reactivity of methyl-hexanoate has been examined and compared to the reactivity of C₄ to C₇ *n*-alkanes in the same experimental conditions to evaluate the impact of the ester function on the reactivity of the *n*-alkyl chain.

Seshadri *et al.* [54] studied the extinction and ignition of non-premixed MD flames in the counterflow configuration. A skeletal mechanism was deduced from the Herbinet *et al.* mechanism [44] using the "directed relation graph" mechanism reduction method. Simulations were found to agree well with experimental data.

In our present study we have carried out a systematic investigation of the fundamental combustion characteristics of lower molecular weight methyl-ester/air mixtures. We have measured the laminar flame speeds and extinction limits of lower molecular weight methyl-ester/air mixtures using the counterflow configuration. Two C₄ (MB and MC) and one C₁₀ (MD) methyl-esters have been considered. The long-term goal of this effort is to contribute towards the development and testing of surrogates and the attendant detailed kinetic

mechanism of methyl-stearate, a methyl-ester with a straight chain saturated hydrocarbon section with 18 carbon atoms, typically found in common biodiesel fuels.

1.1.3 The Formation of Nitrogen Oxides

Combustion processes are the major production source of nitrogen oxides which pose a significant threat to the environment. The principal nitrogen oxides in the atmosphere are nitric oxide (NO) and nitrogen dioxide (NO₂), collectively referred to as NO_x, and nitrous oxide (N₂O). Nitric oxide is emitted even when natural gas or hydrogen are burned because it can be formed at high temperatures from the nitrogen and oxygen from in the air. NO_x in the atmosphere is thought to forms nitric acid, which is a key component of acid rain, and to also contribute to ozone layer depletion and global warming. NO₂ also has a direct impact on health. Because of their relatively short lifetime in the atmosphere, the effect of NO_x tends to be local and regional. On the other hand, N₂O has a long atmospheric lifetime. It reacts with ozone and is the main naturally occurring regulator of stratospheric ozone. Also, it is a major greenhouse gas. Thus, N₂O is a global issue.

Since NO_x and PM emissions from current diesel engines are close to the regulatory limits, and both limits will be even more stringent in the near future, such emissions will be critical factors in the development of new diesel engines. The effect of biodiesel and biodiesel blends on PM and NO_x emissions in diesel engines have been studied by a number of investigators [e.g., [55]-[69]]. Lapuerta *et al* [70], Graboski and McCormick [71], for example, reviewed the body of work on diesel engine emissions when using biodiesel instead of conventional diesel fuels. For PM, a noticeable decrease with biodiesel content represents a universal trend. There is no unanimity, however, about NO_x emissions; most of the technical literature reports an increase in emissions when using a biodiesel fuel, but some studies report NO_x increases only under certain operating condition, while others did not find differences between diesel and biodiesel fuels, and others even found decreases in NO_x emissions.

Various explanations have been offered to account for the increase in NO_x emissions when using biodiesel. They include (i) an advanced injection start when compared to diesel fuel; (ii) the higher Cetane number of biodiesel, which leads to shortening of the ignition delay; and (iii) the higher oxygen content in the combustion chamber when using biodiesel, which could promote the NO formation. As noted above, the chain length and degree of saturation of fatty acid mono-alkyl esters have significant impact on emissions [[65]-[68]]. NO_x emissions increase with increasing fuel density, and an increased number of double bonds correlates with increasing NO_x emissions. For fully saturated FAME, NO_x emissions increased with decreasing chain length. A number of techniques have been proposed, as previously noted, to reduce NO_x emissions from diesel engines when diesel fuel is substituted by biodiesel [[72]-[75]]. They either include a re-adjustment and tuning of the engine, or appropriately selecting and modifying the fuels to be used.

In this study the NO_x emissions of a number model biofuel compounds were investigated in order to develop a better understanding of the processes that lead to NO_x formation and means to minimize such emissions during the use of biofuels. Specifically, we have studied the combustion characteristics of MB and MC and compared with those of *n*-pentane. The NO_x emissions of MD (as a surrogate compound for larger MW FAME) were also studied and compared with those of *n*-decane and *n*-dodecane.

2. Methodology

2.1 Experimental Methodology

The experiments in this study utilize steady, laminar, planar premixed and non-premixed flames that are stabilized in the counterflow configuration (e.g. [[89]-[93]]). A schematic of the experimental set-up is depicted in Fig. 1. For S_u^o determination, the twin flame technique is employed that involves two identical counter-flowing fuel/air jets, thus establishing two symmetrical, planar, near-adiabatic flames. For the premixed extinction and NO_x studies, the configuration involves a N₂ jet counter-flowing against an opposing fuel/air jet resulting in a single premixed flame. The single premixed flame configuration was chosen over the symmetric twin-flame one, because for the same equivalence ratio, ϕ , it results in lower extinction strain rate, K_{ext} , as compared to the twin-flame configuration. Due to the lower strain rates, lower Reynolds numbers are required, and thus the intrinsic flow instabilities are minimized. The diameters of the burner nozzles used are 7 and 14 mm. The separation distance between the burner nozzles is always set equal to the diameter of the burner nozzle used.

Flow field measurements were performed by using the digital particle image velocimetry (DPIV) technique (e.g., [[94],[95]]). DPIV is an optical measurement technique to visualize and characterize flows by measuring the velocities of seeding particles or droplets in the flow of interest. The apparatus consists of a CCD camera, a double-pulsed Nd:YAG laser, a digital pulse generator to synchronize the camera and laser and, thus, control the timing between image exposures, and a series of lenses to convert the laser output into a thin laser sheet. With the illumination of two short duration laser flashes in the measurement area, a doubleexposure of the flow field is captured and the spatially displaced images are stored in two separate frames. The frames are split into a large number of interrogation areas, or windows. It is then possible to calculate a displacement vector for each window with help of signal processing and autocorrelation or cross-correlation techniques. The specific technique used at our facility relies on pattern matching between two successive images of the flow. The displacement field proportional to velocity is obtained from the direct cross-correlation (covariance) between image pairs, limited to small boxes. The displacement vector on each box is determined as the location of the covariance maximum, which is then converted to a velocity using the time between laser shots and the physical size of each pixel on the camera. With the use of DPIV the axial velocity profile along the stagnation streamline is measured, and the absolute value of the maximum velocity gradient just upstream of the flame is determined as the local strain rate, K. In order to determine S_{μ}^{o} , the minimum point of the velocity profile is chosen as a reference upstream flame speed $S_{u,ref}$ corresponding to the imposed stretch rate K, as shown in Fig. 2. Thus, by plotting $S_{u,ref}$ against K, S_u^o can be determined through extrapolation to K = 0 (e.g., [89]-[94]]). In this study, a new nonlinear extrapolation, to be explained later, is used.

 K_{ext} cannot be directly measured due to the fact that at the extinction condition the flow field is unstable. To avoid extrapolations in the determination of K_{ext} , a flame is established for a near-extinction condition, and the prevailing K is measured. Subsequently, the fuel flow rate in the fuel/air jet is slightly modified to achieve extinction [[97],[107]]. For fuellean flames this is done by reducing the fuel flow rate, while for fuel-rich flames, extinction is achieved by increasing the fuel flow rate instead. The modification of the prevailing K due to the slight change in the fuel flow rate has been determined to be inconsequential, and has been shown to be the true K_{ext} both experimentally and numerically. Thus, the reported K_{ext} 's constitute direct measurements. To perform DPIV measurements, the flow was seeded with submicron size silicon oil droplets that are produced by a nebulizer [95].

For the NO_x measurements, sampling was accomplished by continuously withdrawing gases from within the flame using a quartz water-cooled microprobe with an orifice diameter of 100-150 μ m, similarly to Ren *et al* [[96],[97]]. The disturbance to the flame was minimal. The sample was afterwards directed towards a Chemiluminescence NO-NO₂-NO_x Analyzer (Model 42C, Thermo Environmental Instruments Inc., USA), as shown in Fig. 3. The microprobe was mounted on a linear stage, thus allowing it to be vertically adjustable to determine the NOx concentration profile throughout the flame. The positioning system that includes a Cathetometer is established to accurately locate the initial position of the probe (within 25 micrometers), therefore eliminating a major experimental uncertainty. The Chmiluminescence analyzer is of high accuracy with a lower detectable limit of 0.05 ppm.

Although several non-intrusive diagnostic techniques are available, gas sampling and subsequent analysis is a convenient and an inexpensive method for measuring the composition of combustion gases [[98],[99]]. The accuracy of this measurement is determined by the probe design and the setting of the analyzer. In general, the design of the probe has been based on convective cooling or on the aerodynamic quenching techniques. For the convective cooling, water is used to cool down the sampling gas. For the aerodynamic quenching probe, the sampling gas is aerodynamically quenched through a rapid expansion near the probe tip, which is usually achieved in quartz micro probes. In this work, both techniques are applied in the design of the probe.

The design of the probe depends on a number of factors, which depend on the relationship between the characteristic length scales of the probe and characteristic spatial-scales of the flame. The main aerodynamic effect of introducing a probe into a flame results from the disturbance of the scalar concentration gradients in the vicinity of the probe as a result of the streamline distortion. It has been shown [100] that a microprobe in a laminar flow field does not affect significantly the local composition if the sampling is isokinetic. In general [99], the sampling rate and the size of the suction orifice are set as a compromise between the low pressure requirement to achieve aerodynamic quenching of chemical reactions and the minimum flow rate for the chemical analyzers.

The vaporization of the liquid fuels is accomplished by injection into a vaporization chamber, surrounded by heated air similarly to Holley *et al.* [107] and Davis and Law [108]. For this study, an upgraded vaporization system was used, that has the capability to handle heavier liquid fuels, including real biodiesels, as shown in Fig. 4. The stainless steel vaporization chamber used previously was substituted with a glass chamber that allows for visual observations, as needed. Additionally, a quartz nebulizer with a flush capillary lapped nozzle has been integrated into the system to introduce the fuel as a fine aerosol into the chamber. This allows for the complete vaporization to occur in the vapor-phase and also at lower temperatures.

The ratio of liquid fuel to gaseous air or N₂ must be chosen so that the partial pressure of the liquid fuel is maintained below the vapor pressure of the fuel at the prevailing temperature and pressure. Simultaneous heating of the air and the vaporization chamber is required to ensure rapid vaporization and to decrease the time response of the system. The design ensures temperature uniformity throughout the reactant gas lines, all the way to the burner exit. To maintain the fuels in the vapor phase the burners were heated so that the unburned mixture temperature at the burner exit, was $T_u = 333$ K for the studies of methylbutanoate/air and methyl-crotonate/air flames, and $T_u = 403$ K for the studies of methyldecanoate/air flames. All experiments were performed at atmospheric pressures.

2.2 Numerical methodology

 S_u^o 's are computed using the PREMIX code (e.g., [[109],[110]]). The counterflow configuration is simulated using a modified version of the code originally developed by Kee and coworkers [111] to allow for the simulation of asymmetric boundary conditions (e.g., [[112],[113]]). Further modifications were made to account for thermal radiation of CH₄, CO, CO₂, and H₂O at the optically thin limit [112]. Both codes are integrated with the CHEMKIN [114] and Sandia Transport [115] subroutine libraries. Molecular transport was treated using the mixture average formulation and included the influence of the Soret effect.

For the K_{ext} calculations, a vigorously burning flame is first established at a given ϕ and subsequently the K is increased until extinction occurs. At the extinction state, the response of any flame property to K is characterized by a turning-point behavior. This results in a singular point, if *K* is computed as a dependent variable. The code has been modified to solve around this singular point by introducing internal boundary conditions, so that *K* becomes a dependent variable instead of an independent one [116]. Imposing a value for the H radical species concentration at the locations of maximum slopes of the profile, a two-point continuation approach was utilized to solve for *K* [[116],[117]].

Dimethyl-ether/air flames were simulated using the kinetic model developed by Fischer et al. [13] that involves 79 species and 351 reactions. Additionally, an updated kinetic model was used that involves modifications to a number of important reactions pertaining to H₂ and CH₄ chemistry that are explained below. The recent publication by Westbrook et al. [22] contained an updated H_2/O_2 mechanism [119] where the rate constant of Hessler [120] for the $H + O_2 \rightarrow O + OH$ reaction was adopted. However, this has had little effect on the predictions. You et al. [121] have recently reported on the rate constant for the $CO + HO_2 \rightarrow CO_2 + OH$ reaction, which was adopted here as well. Recently, Srinivasan *et* al. [122] studied the $CH_4 + O_2 \rightarrow CH_3 + HO_2$ reaction, and using both experiments and calculations provided a rate constant in the temperature range 1655–1822 K. Jasper et al. [123] have calculated a rate constant expression for the $CH_3 + HO_2 \rightarrow CH_3O + OH$ step that was also adopted here. The rate constant expression for the $C_2H_6 + H \rightarrow C_2H_5 + H_2$ reaction was taken from the GRI-Mech 3.0 [46]. Moreover, sensitivity analysis has shown that ignition delay times for methane, propane, and in particular for ethane are very sensitive to the rate constant for the decomposition of the ethyl radicals to ethylene and H atoms. In this mechanism, the rate constant expression recommended in the GRI-Mech 3.0 [123] was adopted, which is approximately two times slower than the constant previously published for natural gas mixtures [125]. These are the most significant changes, but other minor modifications have also been made to the mechanism, as detailed on the NUI Galway combustion chemistry website <<u>http://www.nuigalway.ie/chem/c3/mechanisms.htm</u>>, which also provides a full listing of the available thermo-chemical and transport parameters.

Methyl-butanoate/air and methyl-crotonate/air flames were simulated using the kinetic mechanism developed by Fisher *et al.* [41] involving 264 species and 1219 reactions and that updated by Gail *et al.* [50] consisting of 295 species and 1498 reactions. Methyl-decanoate/air flames were simulated using the skeletal mechanism, used by Seshadri *et al.* [54], consisting of 125 species and 713 reactions.

Assessing the effects of chemical kinetics and molecular diffusion on S_u^o and K_{ext} requires the use of sensitivity analysis. While the standard CHEMKIN-based codes do allow for automated sensitivity analysis with respect to all rate constants for S_u^o , this is not the case for K_{ext} . In this investigation, this was achieved by invoking the aforementioned two-point continuation approach, so that *K* becomes a dependent variable. As a result, it was possible to perform rigorous sensitivity analysis with respect to rate constants for K_{ext} at the exact location that is determined experimentally, i.e., where it reaches its maximum (absolute) value in the hydrodynamic zone. Furthermore, using a methodology that our group has recently advanced [126], a rigorous sensitivity analysis for both S_u^o and K_{ext} on all binary diffusion coefficients was performed.

Models of nitrogen chemistry are commonly de-coupled from the generalized combustion model and executed after the flame structure has been predicted [127]. The basis for this assumption is that the formation of trace NO_x species does not affect the flame structure, which is governed by the fast fuel-oxidizer reactions. Another advantage of this approach is computational efficiency, since solving the pollutant model equations jointly with the combustion model equations is far more complex. The time required to solve the system of equations for the combusting fuel can require many hours of computer time while the pollutant sub-models typically converge in a fraction of the time required to converge the combustion case. Thus, the NO_x sub-model can be more easily investigated by solving the NO_x sub-model using restart files for a pre-calculated flame structure. The GRI Version 3.0 nitrogen chemistry [80] was coupled into the aforementioned fuel kinetic models to predict the NO_x concentration profiles.



Figure 1. Schematic of experimental set-up for flow-field measurements



Figure 2. Typical axial velocity profile along the centerline and the determination of *K* and

S_{u,ref}.



Figure 3. Schematic of the experimental setup for NO_x measurements



Figure 4. Schematic of the upgraded vaporization system

3. Results and Discussion

3.1 Determination of laminar flame speeds by nonlinear extrapolation

Linear extrapolation of $S_{u,ref}$ to K = 0 has been extensively used to obtain S_u^o in the counterflow flame technique [[89]-[93]]. However, it has been shown both numerically [128] and theoretically [129] that there is a non-linear variation in $S_{u,ref}$ as $K \rightarrow 0$.

Therefore, the linear extrapolation approach can lead to a significant overprediction of S_u° . Subsequent studies have shown that this overprediction can be reduced when larger nozzle separation distances are used to achieve lower *K* [[130],[131]].

In the context of this study, a new non-linear extrapolation technique was developed to determine S_u^o which employs simulations of the opposed-jet experiments. At a given ϕ and nozzle separation distance, the variation of the reference flame speed $S_{u,ref}$ with K was numerically determined with the opposed-jet flow code [[111]-[113]] using the updated mechanism, as shown in Fig. 5. The simulations were terminated at low values of K for which heat loss starts being finite at the boundary. The value of S_u^o at this ϕ , as determined with the PREMIX code, is also shown in Fig. 5 at K = 0. The computed $S_{u,ref}$ at various K's, and the S_u^o at K = 0 were fitted using appropriate polynomials, and it was hypothesized that: (1) the shape of the computed curve provides a close representation of the non-linear behavior at low K's, as it includes realistic description of fluid mechanics, chemical kinetics, and molecular transport; and (2) the shape of this curve (but not necessarily the values) does not depend, to the first order, on uncertainties associated with the kinetics and transport. As shown in Fig. 5, the computed curve over-predicts the experimental data. Subsequently, it was vertically translated to pass through the data and the result from this non-linear extrapolation S_u^o 's at K = 0 are the reported experimental laminar flame speeds. The hypotheses behind this approach were tested by perturbing by $\pm 20\%$ the rate of the main branching reaction $H + O_2 \rightarrow O + OH$, as well as the mass diffusivities of DME and O_2 in the mixture. The results are shown in Fig. 6, and it can be seen that while such perturbations result in distinctly different values of $S_{u,ref}$'s and S_u^o 's, all curves nearly collapse upon vertical translation. This is physically sound, as the balance of momentum and heat at the upstream of the preheat zone, where $S_{u,ref}$ is determined, should not depend to the first order on kinetics and transport. It is also expected, that this approach may provide a more accurate non-linear extrapolation compared to other analyses that are based on assumptions, such as one-step chemistry and simplified transport. As previously noted, the kinetic mechanism to be used in this extrapolation technique does not have to predict the exact values of the laminar flame speeds for a given fuel/air mixture, but it is essential, however, that it accurately predicts the laminar flame speed dependence on equivalence ratio, in order to produce the correct curve shapes.

3.2 Propagation and Extinction of Premixed Dimethyl-Ether/Air Flames

The experimentally determined S_u^o 's are shown in Fig. 7, along with those obtained by other groups. The measured peak S_u^o was determined to be 47 cm/s at $\phi \approx 1.15$. Results reveal that the present data are in close agreement with the recently derived S_u^o 's by Qin *et al.* [20] and Jomaas [21], which we believe are of high quality. The present measurements are considerably lower than those of Zhao *et al.* [19].

Figure 8 shows the experimentally determined S_u^{o} 's along with the numerical simulations using the two aforementioned mechanisms. The Fischer *et al.* [13] mechanism uniformly predicts higher S_u^{o} 's with a maximum discrepancy of about 8 cm/s near the peak. The present updated mechanism predicts slightly higher S_u^{o} 's on the lean side and lower S_u^{o} 's on the rich side. However, the level of discrepancy is considered as moderate.

Figure 9 depicts the experimentally determined K_{ext} as function of ϕ . As expected, K_{ext} exhibits a non-monotonic behavior. The maximum K_{ext} was measured to be 935 s⁻¹ at $\phi \approx 1.2$. This is consistent with the measured S_u^{o} 's, which also peak on the rich side. At the leanest ($\phi = 0.65$) and richest ($\phi = 1.67$) fuel concentrations tested, the experimentally determined K_{ext} 's were 109 s⁻¹ and 179 s⁻¹ respectively. The Fischer *et al.* [13] mechanism uniformly over-predicts the extinction strain rates, with the predicted peak extinction strain rate being nearly 30% higher than the experimental one. The present updated mechanism predicts the experimentally determined K_{ext} 's more satisfactorily. More specifically, it slightly over-predicts the data on the lean side and slightly under-predicts them on the rich side.

To investigate the effect of chemical kinetics and molecular transport on flame propagation, sensitivity analysis was performed using the updated mechanism. Figures 10 and 11 depict the logarithmic sensitivity coefficients (LSC) [110] of S_u^o and K_{ext} to reaction rates for $\phi = 0.6$, 1, 1.5. Since flame propagation and extinction are both high-temperature phenomena, they are both controlled by similar kinetics. Results revealed that DME oxidation is dominated by the main branching reaction,

$$H + O_2 \rightarrow OH + O_2$$

the CO oxidation reaction,

 $CO + OH \rightarrow CO_2 + H$,

and the main termination reaction,

 $H + O_2 + M \rightarrow HO_2 + M$,

similarly to hydrocarbons. Methyl and formyl radicals play also a significant role in DME oxidation, as exhibited by the large LSC's of reactions involving the destruction and production of these radicals. DME decomposition reactions are much less important than methyl and formyl radical reactions. Additionally, it is observed that the LSC's of K_{ext} are uniformly larger, compared to S_u^o , almost across the entire spectrum, which demonstrates that kinetics have a larger influence on flame extinction.

Figures 12 and 13 depict the LSC's of S_u^o and K_{ext} to binary diffusion coefficients for $\phi = 0.6, 1, 1.5$. The LSC of the main branching reaction is also shown for comparison purposes. As expected, S_u^o is found to be sensitive to the binary diffusion coefficients of the major radical species H, O and OH to N₂, major products H₂, CO, H₂O and CO₂ to N₂, and also reactants CH₃OCH₃ and O₂ to N₂. In general, transport exhibits a greater influence on extinction, as observed by the larger sensitivity coefficients of K_{ext} . On the lean side, the LSC of S_u^o to the binary diffusion coefficient of O₂ to N₂ is as large as that to the main branching reaction. This proves the importance of using accurate transport data when validating a kinetic mechanism.

Figures 14-16 depict the integrated species consumption path for freely propagating $\phi = 0.6$, 1.0 and 1.5 flames. At all equivalence ratios, the destruction of DME to methoxymethyl, CH₃OCH₂, is accomplished almost entirely by the free radicals H, O and OH. Methoxymethyl subsequently breaks down to formaldehyde and the methyl radical. Formaldehyde is converted entirely to the formyl radical, followed by conversion into CO and CO₂. This explains the high sensitivities of S_u^o to reactions involving methyl and formyl radicals, which are the intermediates dominating the high temperature DME oxidation kinetics.

3.3 Propagation and Extinction of Premixed Methyl-Ester/Air Flames

The experimentally determined S_u^o 's of methyl-butanoate/air and methyl-crotonate/air mixtures for $T_u = 333$ K are shown in Figs. 17 and 18 respectively, along with detailed numerical simulations using the two aforementioned mechanisms. The peak S_u^o 's measured for methyl-butanoate/air and methyl-crotonate/air mixtures were determined to be 42 cm/s and 43 cm/s, respectively, at $\phi \approx 1.1$. The Fisher *et al.* [41] mechanism appears to over-predict significantly the experimental S_u^o 's, while the revised Gail *et al.* [42] mechanism results in closer agreements.

The experimentally determined S_u^o 's of methyl-butanoate/air and methyl-crotonate/air mixtures at $T_u = 333$ K, are compared in Fig. 19. Both exhibit similar reactivity, although methyl-crotonate/air flames propagate slightly faster. This is expected as a result of the presence of a double bond in the methyl-crotonate molecule.

Experimental and computed S_u^o 's of methyl-decanoate/air flames at $T_u = 403$ K, are shown in Fig. 20. The peak laminar flame speed was determined to be 61 cm/s at $\phi \approx 1.1$. The mechanism overpredicts the experimental S_u^o 's for stoichiometric and rich mixtures.

The effect of the presence of a methyl-ester group in the molecular structure on flame propagation was also assessed. The experimental S_u^o 's of methyl-decanoate/air and *n*decane/air flames at $T_u = 403$ K, are compared in Fig. 21. Methyl-decanoate/air mixtures propagate slower than *n*-decane/air mixtures by an average value of 3.5 cm/s. The lower S_u^o 's are due to the presence of oxygen in the methyl-decanoate molecule leading to lower reactivity.

Figure 22 depicts the experimentally determined K_{ext} 's of methyl-butanoate/air and methyl-crotonate/air mixtures at $T_u = 333$ K. As yet, no numerical results have been obtained for extinction. Due to their similar reactivity, both flames exhibit very similar extinction characteristics, with methyl-crotonate flames exhibiting a slightly higher resistance to extinction. Figure 23 depicts the experimentally determined K_{ext} 's of methyl-decanoate/air and *n*-decane/air mixtures at $T_u = 403$ K. Methyl-decanoate/air flames exhibit a slightly lower resistance to extinction compared to *n*-decane/air flames.

3.4 NO_x Production in Premixed Methyl-Ester/Air Flames

3.4.1 Effect of Oxygen in the Methyl-Ester Molecules

The experimentally determined NO_x concentrations of methyl-butanoate/air, methylcrotonate/air and *n*-pentane/air mixtures at $\phi = 0.8$, 1.0 and 1.2 and T_u = 60 °C are shown in Figs. 24-26. All three flames were at a global strain rate of 168 s⁻¹, defined as twice the nozzle exit velocity divided by the separation distance between the top and bottom nozzles. It can be seen that the NO_x emissions are the highest for methyl-crotonate and lowest for methyl-butanoate on the fuel lean side. It is well known that on the lean side, the NO_x produced from the combustion process is mainly due to the thermal mechanism [23]. Due to the presence of a double bond in methyl-crotonate, more energy is released during oxidation giving the highest flame temperature of the three fuels. Therefore methyl-crotonate/air flames produce the highest levels of NO_x, as expected in Fig. 24.

The experimentally determined NO_x concentrations of methyl-decanoate/air, *n*-decane/air and *n*-dodecane/air mixtures at $\phi = 0.8$, 1.0 and 1.2 and T_u = 130 °C are plotted in Figs. 27-29. All three flames were at a global strain rate of 168 s⁻¹. It can be seen from Fig. 27-29 that the NO_x concentrations of *n*-decane/air and *n*-dodecane/air flames is almost the same for all conditions. This indicates that the NO_x formation and destruction during the combustion process of *n*-decane and *n*-dodecane are similar. For *methyl*-decanoate/air flames, the NO_x concentration is always the lowest when compared to the *n*-decane/air and *n*-dodecane/air flames.

3.4.2 Effect of the chain length

The experimentally determined NO_x concentrations of the methyl-butanoate/air and methyl-decanoate/air mixtures at $\phi = 1.0$ and 1.2 and T_u = 130 °C are plotted in Figs. 30-31. Both flames were at a global strain rate of 168 s⁻¹. The two figures indicate that the NO_x concentrations increase with chain length for the saturated methyl esters.



Figure 5. Representative non-linear behavior of $S_{u,ref}$, with *K*.



Figure 6. Effect of kinetics and transport on the shape of the $S_{u,ref}$, vs. K curve.



Figure 7. Experimentally determined S_u^o 's as a function of ϕ .



Figure 8. Experimentally determined S_u^o 's as a function of ϕ .



Figure 9. Experimentally (symbols) and numerically (lines) determined K_{ext} 's as a



Figure 10. Logarithmic sensitivity coefficients of S_u^o to reaction rates at $\phi = 0.6, 1.0,$



Figure 11. Logarithmic sensitivity coefficients of K_{ext} to reaction rates at $\phi = 0.6$, 1.0, and 1.5.



Figure 12. Logarithmic sensitivity coefficients of S_u^o to binary diffusion coefficients at $\phi = 0.6$, 1.0, and 1.5.



Figure 13. Logarithmic sensitivity coefficients of K_{ext} to binary diffusion coefficients at



Figure 14. Integrated species consumption path for a freely propagating $\phi = 0.6$ flame.



Figure 15. Integrated species consumption path for a freely propagating $\phi = 1.0$

flame.



Figure 16. Integrated species consumption path for a freely propagating $\phi = 1.5$ flame.



Figure 17. Experimentally and numerically determined S_u^o 's of *methyl*-butanoate/air

flames.



Figure 18. Experimentally and numerically determined S_u^o 's for *methyl*-crotonate/air

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Figure 19. Experimentally determined S_u^o 's for *methyl*-butanoate/air and *methyl*-crotonate/air flames.



Figure 20. Experimentally and numerically determined S_u^o 's for methyl

decanoate/air flames.



Figure 21. Comparison of experimentally determined S_u^o 's for *methyl*-decanoate/air and *n*-decane/air flames.



Figure 22. Experimentally determined K_{ext} 's for *methyl*-butanoate/air and *methyl*-crotonate/air flames.



Figure 23. Experimentally determined K_{ext} 's for *methyl*-decanoate/air and *n*-decane/air flames.



Figure 24: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *n*-pentane/air, *methyl*-butanoate/air and *methyl*-crotonate/air flames (equivalence ratio=0.8, K=168 s⁻¹; T_u =60 °C)



Figure 25: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *n*-pentane/air, *methyl*-butanoate/air and *methyl*-crotonate/air flames (equivalence ratio=1.0, K=168 s⁻¹; T_u =60 °C)



Figure 26: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *n*-pentane/air, *methyl*-butanoate/air and *methyl*-crotonate/air flames (equivalence ratio=1.2, K=168 s⁻¹; T_u =60 °C)



Figure 27: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *n*-decane/air, *n*-dodecane/air and *methyl*-decanoate/air flames (equivalence ratio=0.8, $K=168 \text{ s}^{-1}$; $T_u=130 \text{ °C}$)



Figure 28: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *n*-decane/air, *n*-dodecane/air and *methyl*-decanoate/air flames (equivalence ratio=1.0, $K=168 \text{ s}^{-1}$; $T_u=130 \text{ °C}$)



Figure 29: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *n*-decane/air, *n*-dodecane/air and methyl decanoate/air flames (equivalence ratio=1.2, $K=168 \text{ s}^{-1}$; $T_u=130 \text{ °C}$)



Figure 30: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *methyl*-butanoate/air and *methyl*-decanoate/air flames (equivalence ratio=1.0, K=168 s⁻¹; T_u =130 °C)



Figure 31: Experimentally determined NO_x concentration profiles as a function of distance from the bottom burner for *methyl*-butanoate/air and *methyl*-decanoate/air flames (equivalence ratio=1.2, K=168 s⁻¹; T_u =130 °C)

4. Conclusions and Future Work

In this study, we have focused our attention on a number of model biofuels specifically dimethyl-ether (DME), a very promising clean fuel that can be derived through processing of biomass-derived syngas, and several low MW methyl-esters as surrogates of fatty acid methyl-ester (FAME) type biofuels. We have studied the fundamental combustion characteristics of these fuels, as well their pollutant emissions, particularly nitrogen oxides (NO_x). In this Final Report we provided a brief description of the work that we carried out as part of our METRANS funded project. The following is a brief overview of our key technical contributions and findings.

- Our study provided further insight into the combustion characteristics of DME and its high temperature kinetics and resolved a number of issues that remained unresolved pertaining to both the experiments as well as the modeling of DME flames. Laminar flame speeds and extinction limits of DME/air mixtures were measured using the counterflow configuration. These measurements were compared to published experimental data and to numerical simulations using an updated kinetic model. Sensitivity and reaction pathway analyses were conducted which provided insight into the controlling physico-chemical processes.
- The laminar flame speeds and extinction limits of two C₄ (MB and MC) and one C₁₀ (MD) methyl-esters were experimentally measured and numerically analyzed. Such data and simulations are important key first step towards meeting the long-term goal of the development and testing of surrogates and the attendant detailed kinetic mechanism of methyl-stearate, a methyl-ester with a straight chain saturated hydrocarbon section with 18 carbon atoms, typically found in common biodiesel fuels.
- The NO_x emissions of MB and MC were measured and numerically simulated and compared with those of *n*-pentane. The NO_x emissions of MD (as a surrogate compound for larger MW FAME) were also studied and compared with those of *n*-decane and *n*-dodecane. These studies have helped us develop a better understanding of the processes that lead to NO_x formation and means to minimize such emissions during the use of biofuels.

Future work, which is supported by grants from NASA and DOE which were secured using the METRANS support as seed-funding, will include:

4.1 Investigation of the Flow Field in Counterflow Flames

The remaining work includes a careful investigation of the flow field in counterflow flames and the validity of assumptions made in the direct numerical simulations of the experiments.

4.2 **Temperature measurements**

Current experimental data shows that the NO_x emissions of biofuels are lower than that of *n*-alkanes at the same equivalence ratio. As reported in the literatures, the NO_x emissions on the lean side of the flames are due to the thermal or Zeldovich mechanism. Thus, studying the temperature profile during the combustion process of biofuels, especially on the fuel lean side will provide useful insights in the effect of oxygen of the biofuel combustion process.

4.3 Simulations of the *methyl*-ester stagnation flames including path analyses

The simulations of the methyl-ester stagnation flames will be completed using skeletal versions of the full mechanisms obtained using a directed relation graph. These simulations will be for both the NO_x profiles and extinction. Also, studies of path and sensitivity analysis will be used to investigate the differences between the NO_x emissions of biofuel and *n*-alkane combustion process. Different NO_x mechanisms coupled with the generalized combustion model along with the path and sensitivity analysis will be studied to compare with the experimental data.

4.4 Studies of extinction and NO_x emissions in non-premixed flames

From a practical viewpoint, diffusion flames can exhibit significant differences in flame structure compared to the premixed flame. Non-premixed extinction data also need to be obtained for dimethyl-ether and methyl-ester flames to test the validity of the mechanism in non-premixed flames. The extended high-temperature post-flame region of premixed flames favors NO formation via the thermal mechanism. In the modeling study of opposed flow $CH_4/N_2/air$ diffusion flames, Drake and Blint [77] and Nishioka [132] reached the similar conclusion that the two primary contributions to NO formation are thought to arise from this route and the prompt mechanism. Thus, it is interesting to investigate the NO_x formation and destruction in diffusion biofuel flames.

4.5 Effect of oxygen availability and strain rate

As reported in the report, the oxygen presence in the saturated methyl esters can affect the NO_x emissions during the combustion process. Another way to investigate the effect of oxygen in *methyl*-esters flames is to study the NO_x emissions of the mixtures of conventional diesel fuel and oxygen with the same hydrocarbon/oxygen molar ratio as that of the biofuel. Studies of NO_x emissions of biodiesels in an engine by Lapuerta *et al.* [[133],[134]] concluded that the oxygen content of biodiesel could not be the cause of any increase in NO formation because diffusion combustion occurs mainly in regions with an approximately stoichiometric oxygen-fuel ratio. Additional studies are needed, however, under wellcontrolled experimental conditions to provide conclusive answers on this issue. Studies of premixed and non-premixed flames will also be carried out to investigate NO_x emissions under different flame strain rates.

5. **References**

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