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A shock tube and laser absorption study of CO time-histories during bio-ether oxidation and pyrolysis

Andrew R. Laich[1], Erik M. Ninnemann[1], Owen M. Pryor[1, *], Sneha Neupane[1], and Subith S. Vasu[2]
[1]*Center for Advanced Turbomachinery and Energy Research (CATER), Department of Mechanical and Aerospace Engineering, University of Central Florida, Orlando, FL 32816*

[*]*Southwest Research Institute*
San Antonio, TX 78238

The chemical kinetics of propyl methyl ether (PME), a proposed biofuel, has been studied behind reflected shock waves near 10 atm over a temperature range of 1200 – 1525 K. Mixtures consisting of 0.1% PME/0.6% oxygen and 0.5% PME were used to investigate pressure and CO time-histories during PME oxidation and pyrolysis in argon, respectively. Carbon monoxide mole fractions were measured behind reflected shock waves with a continuous wave quantum cascade laser centered at 2046.30 cm^{-1} using fixed-wavelength direct absorption spectroscopy.

Introduction

Given strict emission regulations and a growing energy demand reliant on fossil derived fuels, the implementation of biofuels has the capability of mitigating adverse environmental effects that have arisen from burning these fossil fuels. Benefits of carbon neutrality, a reduction in harmful emissions, and improved efficiency can be realized in future engine developments compatible with these fuels.

Ether compounds, as a transportation fuel, are an attractive option as they can be used as additives or stand-alone biofuels [1]. Propyl methyl ether (PME) is one such potential candidate (scheme 1). Previous combustion related studies do not include PME; however, a similar isomeric ether of PME, diethyl ether (DEE), has been studied in the literature. Some of these studies include oxidation/pyrolysis experiments in a shock tube [2] and jet-stirred reactor [3, 4], as well as ignition delay time measurements in a rapid compression machine (RCM) [5]. Yasunaga et al. [2] performed shock tube oxidation and pyrolysis experiments on DEE between 900 – 1900 K and 1 – 4 atm. This work included the assemblage of a chemical kinetics model from a base mechanism. Major products including carbon monoxide (CO) and acetaldehyde were obtained through gas chromatography sampling. Werler et al. [5] measured ignition delay times in a shock tube at temperatures between 900 – 1300 K and at pressures of 10, 20, and 40 bar. This work also included RCM experiments at 500 – 1060 K and pressures between 2.5 to 13 bar. Simulations based on the Yasunaga et al. detailed chemical mechanism were compared to experiment. During RCM studies the authors observed two-staged ignition at temperatures between 500 – 655 K. Serinyel et al. [3] performed oxidation experiments in a jet-stirred reactor where strong low temperature chemistry at high pressure was observed.

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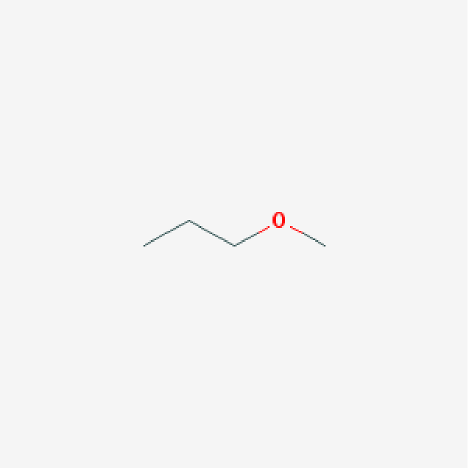
[1] Graduate Student, University of Central Florida, Orlando, Fl 32816, Student Member
[2]Associate Professor, CATER, University of Central Florida, Orlando, FL 32816, Associate Fellow



Scheme 1- PME structure (source: https://pubchem.ncbi.nlm.nih.gov/).

In the present work, we have examined the oxidation and pyrolysis of PME behind reflected shock waves between temperatures of 1200 to 1525 K and pressures between 8.5 to 10 atm.

I. Experimental Procedure

Carbon monoxide time-histories were measured in the stainless, double-diaphragm, and heated shock tube facility at the University of Central Florida (UCF), specific details of which can be found in Koroglu et al. [6-14]. Both driver and driven sections have an inner diameter of 14.17 cm. Separating the two sections is a Lexan diaphragm, which bursts upon the filling of gas in the driver section creating a normal shockwave. Approximately 2.00 cm from the end-wall are machined ports, several of which house a window that allows optical access for an emission detector, laser diagnostics, and pressure probes. The incident shock velocity is measured using four Agilent 53220A timer counter boxes linked to five equally spaced PCB 113B26 piezoelectric pressure transducers along the last 1.5 m of the driven section. The quasi one-dimensional normal shock relations and calculated incident-shock velocity were utilized to determine temperature (T_5) and pressure (P_5) behind reflected shock waves. Time-zero for these experiments is defined as the minimum point of the Schlieren spike of the CO laser trace, upon reflection of shock wave.

Time-resolved measurements of carbon monoxide were measured using a continuous wave quantum cascade laser (Alpes QCL) with a fixed-wavelength direct absorption measurement technique at 2046.30 cm^{-1}. According to the model the top forming species include oxygen, water, carbon dioxide, formaldehyde, ethylene, acetylene and methanol – none of which present significant interference at the wavelength chosen for measuring CO formation. Experimental mole fractions of carbon monoxide were obtained by using the Beer-Lambert Law,

$$X_{CO} = \frac{\alpha RT}{\sigma PL}$$

where

$$\alpha = -\ln\left(\frac{I}{I_0}\right)$$

is the absorbance, R is the universal gas constant (cm^3*atm/K*mole), T is the temperature of the gas (K), σ is the absorption cross-section of the absorbing species (cm^2/molecule), P is the total pressure of the gas (atm), and L is the path length (cm). In the absorbance expression, I and I_0 are the transmitted and reference laser signals, respectively, which can be seen in Fig. 1 for a typical oxidation shock tube experiment. These signals were obtained by the focusing of laser light onto thermoelectrically cooled HgCdTe (MCT) detectors (Vigo Systems, PVI-2TE-5). The absorption cross-section for carbon monoxide was determined experimentally by shock heating a mixture of 1% CO+12% He in argon, where an empirical relation was developed for validity within targeted experimental conditions. The absorption cross-section obeys a power law fit for both temperature and pressure at the chosen line.

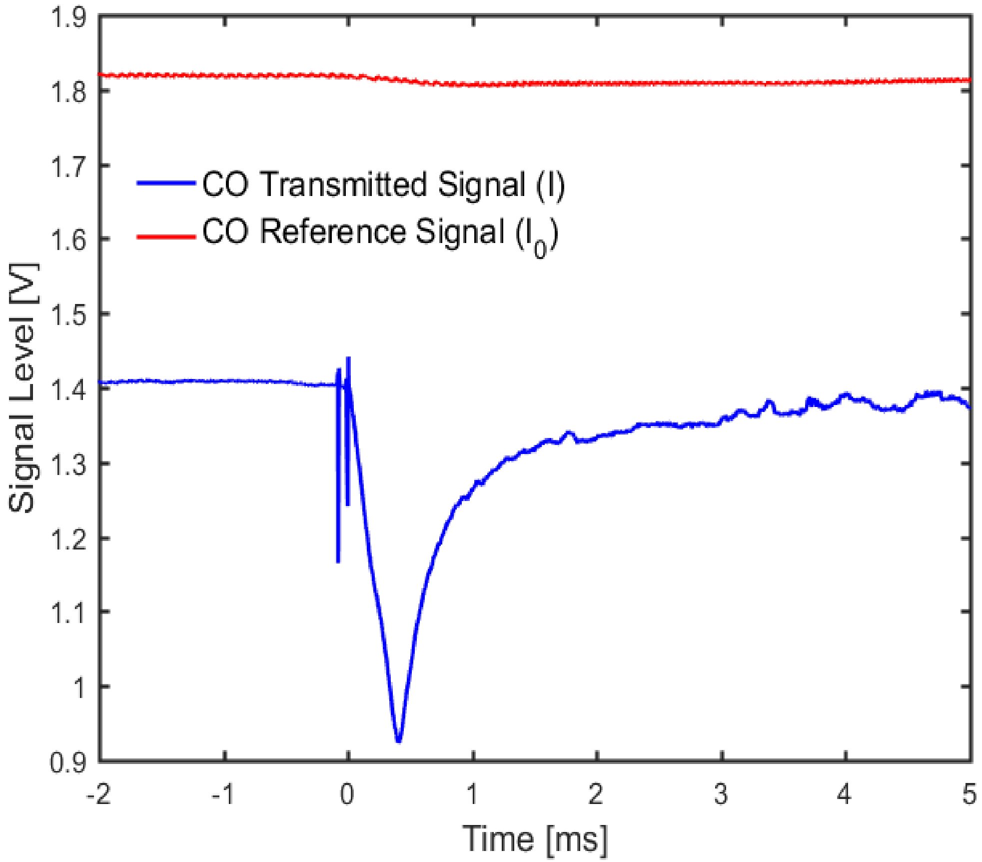


Figure 1. Raw transmitted and reference signals with shown schlieren spikes in I (blue) during incident and reflected shock waves, followed by a decrease in signal (absorption) due to CO formation.

The propyl methyl ether mixture in this study was prepared manometrically with two MKS Baratrons of full-scale range 100-Torr (E27D, accuracy of 0.12%) and 20000-Torr (628F, accuracy of 0.25%). The mixture was contained in a 33L Teflon-coated mixing tank fitted with a magnetically driven stirrer, which was left to mix for at least one hour before use. To verify initial fuel concentration in the mixture, FTIR measurements of PME were taken using the FTIR set-up spectroscopy at UCF, as detailed in [13]. Cross-section measurements were performed over a wavelength range of 449.34 – 4001.63 cm^{-1} with a resolution of 1.9285 nm, path length of 10 cm temperature of 296 K and pressure of 5.53 Torr. Using this cross-section data, laser absorption spectroscopy was employed to verify the fuel concentration near 3.49µm (2938.25 cm^{-1}) at the beginning of each shock tube experiment.

II. Results and Discussion

Pressure and CO time-history measurements of PME oxidation and pyrolysis behind reflected shock waves were taken around 1200 – 1525 K and 8.5 – 10 atm. Pressure traces and CO time-histories were captured for all shocks that were performed, and a typical representation of this is shown below in Fig. 2 with an uncertainty band for CO time-histories. The pressure traces during oxidation/pyrolysis initially have an upward linear trend, however, this will have negligible effect on the measured CO and such considerations have been included in the uncertainty estimates.

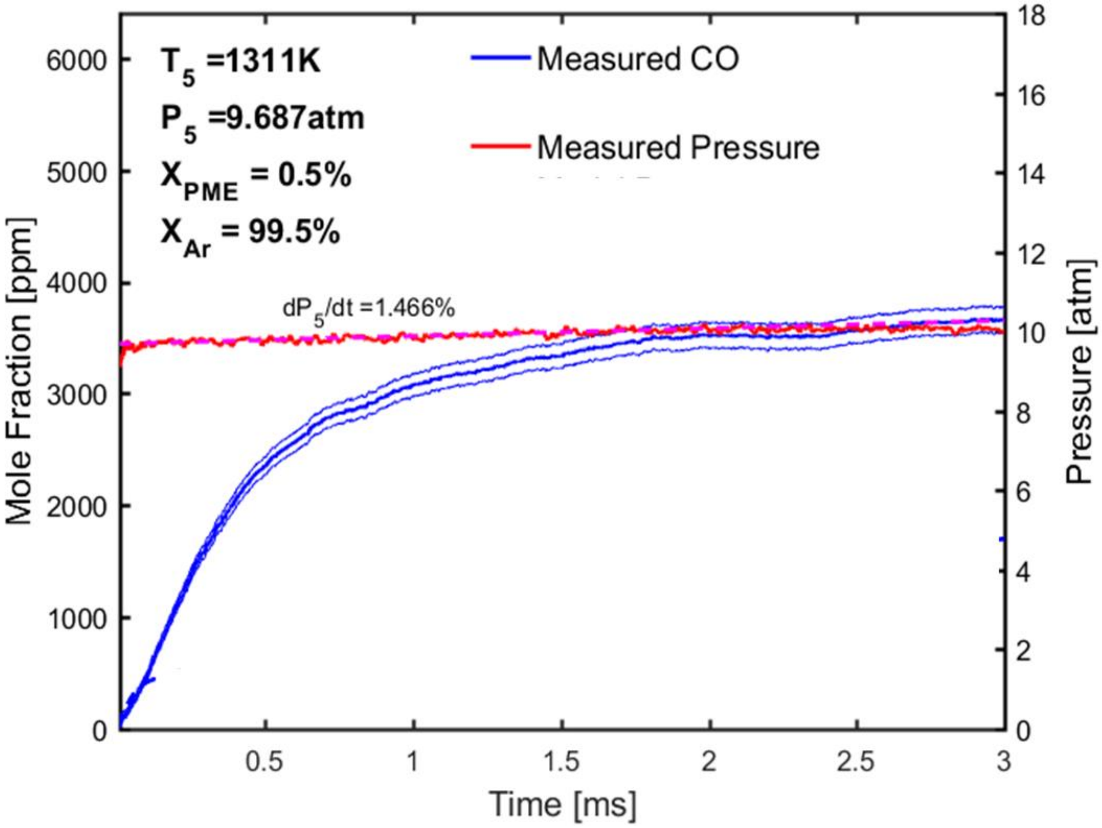


Figure 2. Pressure trace and CO time-history during the pyrolysis of 0.5% PME at 1311K and 9.7atm.

III. Summary

Oxidation and pyrolysis experiments of PME, a proposed biofuel, were performed in a shock tube. Carbon monoxide time histories were measured in the infrared near 4.9 µm with laser diagnostics developed and characterized in-house for validity within the specified experimental conditions. Future work will include formaldehyde time-histories and ignition delay time measurements. Current data will aid in the development of validated chemical kinetic mechanisms for PME.

IV. Acknowledgements

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