

A FUNDAMENTAL STUDY OF THE OXIDATION CHARACTERISTICS AND POLLUTANT EMISSIONS OF MODEL AND REAL BIODIESELS

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Summary

The oxidation characteristics of several model and real biodiesel fuels are investigated. The goal of the study is to contribute towards the fundamental understanding of biodiesel combustion, and to evaluate the effect of using these alternative fuels on engine performance as well as on the environment. In addition to several commercial biodiesels, this study also included several pure methyl-esters that can serve as surrogate compounds for such fuels, ranging from C₄ methyl esters, such as methyl butanoate and methyl crotonate, to C₁₈ methyl esters, such as methyl stearate. The experiments were conducted at ambient pressure and elevated temperatures over a wide range of fuel/oxidizer ratios. Laminar flame speeds and extinction limits were determined in the stagnation-flow configuration using digital particle image velocimetry. The effects of chain length and degree of saturation on the fundamental flame properties of these fuels were evaluated. NO_x concentration profiles were measured in stagnation flow flames by sampling using a quartz micro-probe followed by chemiluminescence analysis. Several large detailed chemical kinetic mechanisms were tested against the experimental data in order to provide insight into the high-temperature oxidation kinetics of these methyl esters.

Keywords

Oxidation of Biodiesels, Laminar Flame Speeds, Extinction Limits, NO_x Emissions

Introduction

The world faces today the threats of a potentially crippling energy crisis and of serious emerging environmental problems. Biodiesel is one of the most viable and affordable solutions for reducing the dependence on conventional petroleum.

Biodiesel is a multiple-component mixture of mono-alkyl esters of long-chain fatty acids derived from vegetable oils and/or animal fats. Biodiesel can be used either pure or as a mixture with conventional petroleum diesel. Compared to conventional diesel, biodiesel can serve as a cleaner fuel, with lower emissions of CO, CO₂, sulfur oxides, and of particulate matter (PM).

There have been studies in diesel engines of the emissions of PM and nitrogen oxide (NO_x) resulting from the combustion of biodiesel and biodiesel blends. Most of these studies demonstrate that PM emissions of biodiesel /conventional diesel blends decrease noticeably as the biodiesel content increases. However, different conclusions were reached concerning the effect of biodiesel on the NO_x emissions. Some studies [e.g., 1] have shown an increase in NO_x emissions when using biodiesel fuel. Others [e.g., 2] found no difference between diesel

and biodiesel fuels, while a third group [e.g., 3] has found decreases in NO_x emissions

Unfortunately, despite its potential for use as a practical fuel, the combustion characteristics of biodiesel are, as yet, neither well characterized nor well understood. Therefore, it is essential today to further advance the understanding of biodiesel combustion and to evaluate the consequences of its use on both engine performance and the environment. At present, fundamental data and chemical kinetic models describing the behavior of actual biodiesels are not available. However, some studies have appeared on lower molecular weight (MW) alkyl esters that may be considered as model surrogate compounds in place of the complex biodiesels. Fisher *et al* [4], for example, published a chemical mechanism for methyl butanoate (MB) using low temperature oxidation data in an isothermal static reactors. Gail *et al.* [5] subsequently updated the MB mechanism and used it to simulate experimental results in jet stirred reactors and diffusion flames. More recently, a kinetic mechanism was developed by Herbinet *et al* [6] and was used to study the oxidation of methyl decanoate (MD), potentially a more

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realistic surrogate for biodiesel fuels. The extinction and ignition characteristics of non-premixed MD flames were studied by Seshadri *et al.* in the counterflow configuration [7]. The goal of the present work, therefore, is to systematically study the fundamental combustion and emission characteristics of both real and model biodiesels, and to understand the chemical differences that are at the root of their combustion performance.

Results

Our study involved the measurement of laminar flame speeds, S_u^o , extinction characteristics, and pollutant (PM and NO_x) emissions in the stagnation-flow configuration. The effects of chain length and degree of saturation on the fundamental flame properties of these fuels were evaluated. The experimentally determined S_u^o 's of MB/air flames at atmospheric pressure and 60 °C are shown, for example, in Fig. 1, along with detailed simulations using the aforementioned two published mechanisms [4,5]. The peak S_u^o 's for the MB/air flame was determined to be 42 cm/s at $\phi \approx 1.1$. The Fisher *et al.* mechanism [4] appears to significantly overpredict S_u^o 's, while the revised Gail *et al.* [5] mechanism results in closer agreement.

Figure 2 compares the experimentally determined extinction strain rates (K_{ext}) of MD/air and *n*-decane/air mixtures at ambient pressure and at 130 °C. MD/air flames exhibit a slightly lower resistance to extinction when compared to *n*-decane/air flames.

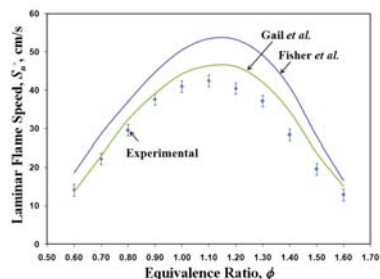


Figure 1. S_u^o 's of premixed MB/air flames.

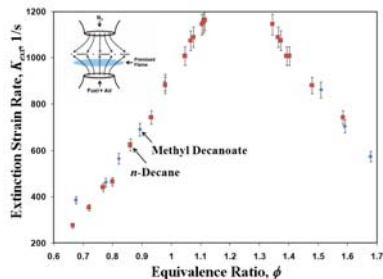


Figure 2. K_{ext} 's of MD/air and *n*-decane/air mixtures

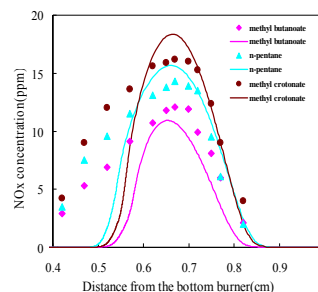


Figure 3. NO_x profiles for *n*-pentane/air, MB/air and MC/air flames (equivalence ratio=0.8, $K=168 \text{ s}^{-1}$; $T_u=60 \text{ }^\circ\text{C}$)

Figure 3 compares the NO_x concentrations of MB/air, methyl crotonate (MC)/air and *n*-pentane/air mixtures at ambient pressure and at 60 °C. Satisfactory agreements were observed between the model and the experiments in the flame and the post-flame regions. The MC/air flame produces the highest level of NO_x due to the double bond in its molecular structure, while the MB/air flame has the lowest NO_x concentration of all three model fuel.

Conclusions

Laminar flame speeds, extinction characteristics, and pollutant emissions in the stagnation-flow configuration were experimentally determined for a wide range of equivalence ratios at elevated temperatures for both model and real biofuels. The fundamental flame properties of these fuels were shown to depend sensitively on the molecular structure, including the chain length and the number of double bonds. NO_x measurements with model biodiesels indicate that compounds with double bonds result in higher NO_x emissions than either the saturated methyl esters or the more conventional fuels (straight chain alkanes). Additional data, including PM formation, will be presented at the meeting.

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