

Ignition Delay and Pyrolysis in Methyl Esters

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Motivation

Diesel fuel is a vital energy source in the United States power generation and transportation industries due to its potential for increased efficiency and reliability. However, it faces a number of challenges, including higher nitric oxide (NO_x) and particulate matter (PM) emissions (U.S. EPA, 2003), and more stringent emissions regulations (Federal Register, 2001). Moreover, the United States is dependent on a finite supply of imported fossil fuel (Fisher, 2000) (Metcalf, 2007). The infrastructure to burn diesel fuel is in place, but the fuel itself is becoming impractical. A substitute is needed (Knothe, 2007).

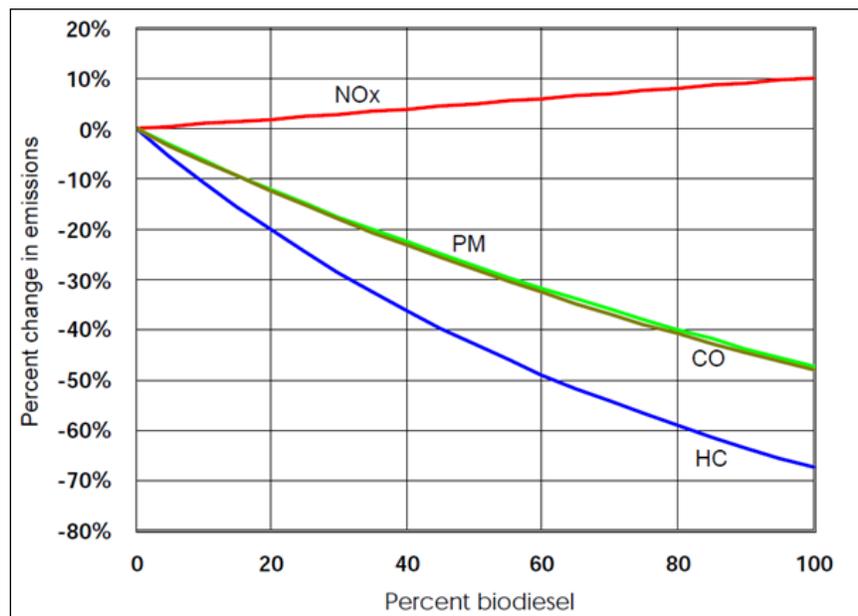


Figure 1: Relative to fossil diesel, biodiesel shows noticeable decreases in particulate matter, carbon monoxide, and hydrocarbon emissions, but often shows an increase in nitrogen oxides (U.S. EPA, 2002)

Biodiesel is one such replacement. This renewable oxygenated fuel can be grown and processed entirely in the United States (Yanowitz, 2009), and is known to drastically reduce hydrocarbon, particulate matter, and carbon monoxide emissions in heavy trucks (see Figure 1) (U.S. EPA, 2002). However, an increase of emitted nitric oxide of up to 10.5% for neat biodiesel compared to fossil diesel is still not fully explained (Graboski, 1998) (Cheng, 2006) (Knothe, 2007) (Zhang, 2007) (Yanowitz, 2009). Further, detailed data of biodiesel pyrolysis and oxidation for mechanism validation is scarce. In order to design diesel engines that can capitalize on biodiesel's benefits without compromising emissions, we must gain a fundamental understanding of biodiesel ignition timing and exhaust formation through kinetic species time-history trials (Graboski, 1998) (Herbinet, 2008).

Current measurements

Currently, the Hanson Group is conducting experiments to understand pyrolysis (molecular breakup) and ignition delay (time between pressure increase and detonation) of biodiesel surrogates (fuels similar in nature to biodiesel) in the aerosol shock tube (AST). For most fuels with high vapor pressures, a standard shock tube is able to make accurate measurements of these quantities. However, biodiesel vapor pressures are much lower, necessitating use of the AST. The AST functions by creating an aerosol out of the fuel, drawing it into the tube, evaporating it, and then shocking it into ignition.

Biodiesel is composed primarily of five large methyl esters (see Table 1). Methyl oleate, methyl linoleate, and methyl linolenate are all liquids at room temperature, while methyl palmitate and methyl stearate are solids. Tests in the aerosol shock tube have successfully been performed with all methyl esters except methyl linolenate, which is difficult to obtain in large quantities at high purity. Sample data for methyl linoleate ignition is given in Figure 2.

Table 1: Composition of two common biodiesels (Herbinet, 2008)

Ester	Soybean Biodiesel	Rapeseed Biodiesel
Methyl palmitate ($C_{17}H_{34}O_2$)	6-10%	4.3%
Methyl stearate ($C_{19}H_{38}O_2$)	2-5%	1.3%
Methyl oleate ($C_{19}H_{36}O_2$)	20-30%	59.9%
Methyl linoleate ($C_{19}H_{34}O_2$)	50-60%	21.1%
Methyl linolenate ($C_{19}H_{32}O_2$)	5-11%	13.2%

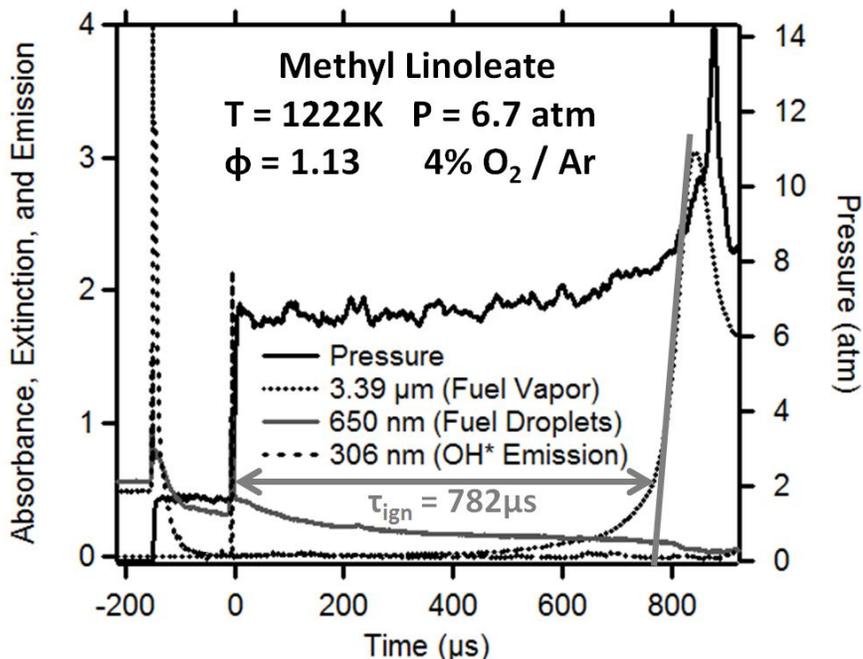


Figure 2: Methyl linoleate ignition delay time measurement in the aerosol shock tube (Campbell, 2013)

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