Scaling relation for high-temperature biodiesel surrogate ignition delay times

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Abstract

High-temperature Arrhenius ignition delay time correlations are useful for revealing the underlying parameter dependencies of combustion models, for simplifying and optimizing combustion mechanisms for use in engine simulations, for scaling experimental data to new conditions for comparison purposes, and for guiding in experimental design. We have developed a scaling relationship for Fatty Acid Methyl Ester (FAME) ignition time data taken at high temperatures in 4%O₂/Ar mixtures behind reflected shocks using an aerosol shock tube:

$$\tau_{ign} [\text{ms}] = 2.24 \times 10^{-6} [\text{ms}] (P [\text{atm}])^{-0.41} (\phi)^{0.30} (C_n)^{-0.61} \exp\left(\frac{37.1 [\text{kcal/mol}]}{\hat{R}_u [\text{kcal/mol-K}] T [\text{K}]}\right)$$

Additionally, we have combined our ignition delay time data for methyl decanoate, methyl palmitate, methyl oleate, and methyl linoleate with other experimental results in the literature in order to derive fuel-specific oxygen-mole-fraction scaling parameters for these surrogates. In this article, we discuss the significance of the parameter values, compare our correlation to others found in the literature for different classes of fuels, and contrast the above expression's performance with correlations obtained using leading FAME kinetic models in 4%O₂/Ar mixtures.

Keywords: Shock tube, Ignition delay time, Fatty Acid Methyl Ester (FAME), Biodiesel surrogate, Correlation

PACS: 88.85.mb, 82.33.Vx

10 **2010 MSC:** 80A25, 80A30

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Preprint submitted to Fuel Journal

September 27, 2015

20 1. Introduction

Increasingly stringent regulations for heavy-duty diesel engine exhaust have led manufacturers to search for methods of reducing nitrogen oxide (NO_x) and particulate matter (PM) emissions [1–3]. Such techniques include Exhaust Gas Recirculation (EGR), in which a portion of the exhaust gases are combined with the pre-combustion fuel/air blend in order to decrease the oxygen content of the mixture and hence reduce NO_x [4, 5], and blending fossil diesel fuel with small fractions of biodiesel fuel, which can reduce PM [6–10]. However, these prevention techniques are complicated by the fact that EGR sometimes results in increased exhaust PM [4, 5], and in some engines biodiesel has been linked with increased levels of tailpipe NO_x [6–12]. Thus, care must be taken in using EGR and biodiesel in conjunction [13]. This motivates a thorough understanding of biodiesel combustion in lower-oxygen-content ($\leq 21\%$) mixtures.

Shock tube ignition delay times are a critical component for developing and validating combustion models [14–17]. These models are used to evaluate fuel blends and design diesel engines [18–26]. High-temperature shock tube ignition delay time data can be summarized by correlations that serve to reveal the underlying dependence of ignition times on important parameters such as pressure or equivalence ratio [27]. Such correlations are useful for simplifying/optimizing combustion models for use in diesel engine Computational Fluid Dynamics (CFD) simulations, for scaling experimental data to new conditions for comparison purposes, and for guiding in experimental design [28–32]. Several authors have suggested high-temperature

Arrhenius-like correlations for various fuels (normal alkanes, oxygenates, *etc.*), including those
 40 listed in References [27, 33–46] (see also Table 1). Other more complex ignition delay time correlations have also been suggested that cover both high and low temperatures [47–49]. However, we are unaware of any such correlation for large biodiesel surrogates at high temperatures and low oxygen concentrations; this provides motivation for the present work.

[Table 1 about here.]

45 2. Previous biodiesel ignition studies

Recently, our research group published two articles containing high-temperature ignition delay times measured in 1%, 4%, and 21% oxygen/argon mixtures behind reflected shock waves in an aerosol shock tube for a series of biodiesel surrogate molecules in the Fatty Acid Methyl Ester (FAME) family [50, 51]. These fuels included methyl decanoate (MD, $C_{11}H_{22}O_2$; see Fig-
 50 ure 1), which was measured at 1% and 21% oxygen mole fractions, and methyl laurate (MLA, $C_{13}H_{26}O_2$), methyl myristate (MM, $C_{15}H_{30}O_2$), methyl palmitate (MP, $C_{17}H_{34}O_2$), methyl oleate (MO, $C_{19}H_{36}O_2$), and methyl linoleate (ML, $C_{19}H_{34}O_2$), which were measured in 4% oxygen mixtures. Importantly, the fact that these shock tube studies were performed at oxygen concentrations at or below 21% allows these experiments to serve as a proxy for EGR behavior. Our
 55 first goal in this work was to use these two data sets to develop an ignition delay time correlation for large FAMEs in 4% O_2 /Ar mixtures that captures the effects of temperature T , pressure P , equivalence ratio ϕ , molecular size (carbon chain length) C_n , and, if necessary, hydrogen unsaturation (number of C=C double bonds) U_d . Moreover, our second ambition was to synthesize other FAME ignition delay data available in the literature [45, 46, 52–60] in order to develop
 60 scaling parameters for the dependence of ignition time on the mixture oxygen mole fraction x_{O_2} .

[Figure 1 about here.]

[Table 2 about here.]

Before proceeding, we wish to note that other shock tube studies have specifically simulated
 65 EGR conditions by adding $CO_2/H_2O/O_2/N_2$ blends to the pre-shock mixture [48, 55, 61]. However, these works do not include experimentation at oxygen concentrations as low as used in our

studies [50, 51]. Also, it should be mentioned that many shock tube studies are performed with fuel/oxygen mixtures that are diluted in argon rather than in nitrogen [29]. The effects of the choice of diluent are well-understood and thus will not be considered here [62].

70 3. Experimental methods

Complete experimental details for our previous biodiesel studies can be found in References [50, 51, 63]; therefore, only a brief overview will be given here. All ignition delay shock-tests were conducted using the Stanford University Aerosol Shock Tube (AST). Experimental conditions are summarized in Table 2.

75 The AST uses a series of gate valves and pressure differentials to deliver a spatially uniform aerosol of micron-sized fuel droplets suspended in a carrier gas consisting of oxygen, argon, and fuel vapor into the last meter of the shock tube driven section. An incident shock wave, generated via strain-induced rupture of a diaphragm by high-pressure helium in the driver section, passes through the aerosol, causing the droplets to evaporate and diffuse into the carrier gas; this creates
80 a uniform premixed combustion environment. When the incident shock wave reaches the endwall of the tube, it reflects and passes through the premixed gas, compressing and heating it to the temperature and pressure of the combustion experiment, known as T_5 and P_5 , respectively.

A helium-neon laser passing through the shock tube at a distance of approximately 3 cm from the endwall is used to measure the equivalence ratio of the mixture (see also References [64, 65]).
85 Ignition delay times are marked by the emission from kinetically excited OH radicals (OH^*) at 306 ± 75 nm, also at an endwall distance of 3 cm. Uncertainties in ignition times are typically $\pm 30\%$, conservatively estimated by considering individual error contributions from temperature ($\pm 1\%$), pressure ($\pm 2\%$), and equivalence ratio ($\pm 7\%$) [63].

4. Analysis

90 4.1. Ignition delay correlation

For our analysis we chose to use the ignition delay time τ_{ign} correlation of Davidson *et al.* [42]:

$$\tau_{ign} = AP^a \phi^b C_n^c \exp\left(\frac{\hat{E}_A}{\hat{R}_u T}\right) \quad (1)$$

In this expression, input values are temperature T [K], pressure P [atm], equivalence ratio ϕ , and molecular size (carbon chain length) C_n . Fitting parameters include $a/b/c$ (the fitting exponents), the A-factor A [ms], and the activation energy $\hat{E}_A$ [kcal/mol]; $\hat{R}_u = 1.987 \times 10^{-3}$ [kcal/mol-K] [66, 67] is the ideal gas constant. Among the available correlations found in the literature
 95 (see several in Table 1), Equation 1 is advantageous because its input values are directly measured/controlled experimental parameters and also its form is similar to Arrhenius reaction rate constant expressions [27, 29]. The importance of fuel hydrogen saturation (number of C=C double bonds) will be discussed in Section 4.2.

We fit Equation 1 to our $x_{O_2} = 0.04$ ignition delay time data for MLA, MM, MP, MO, and
 100 ML while accounting for experimental uncertainties in T , P , and ϕ . This was made possible using Igor Pro software combined with the ODRPACK95 algorithm for Orthogonal Distance Regression (ODR) [68–70]. Fuel impurities and uncertainties in mixture composition were small and thus not considered. Fitting coefficients derived using this method are presented in Table 3, together with standard errors ($\pm$ values).

105 [Table 3 about here.]

While ODR can account for errors in fitting inputs, it is not able to provide a value for the coefficient of multiple determination (R^2) or supply p -values for indicating the importance of the fitting parameters. Thus, we used the R statistics program with the MASS package [71, 72] to analyze the logarithm of Equation 1,

$$\ln(\tau_{ign}) = \ln(A) + a \ln(P) + b \ln(\phi) + c \ln(C_n) + \frac{\hat{E}_A}{\hat{R}_u} \left(\frac{1}{T} \right) \quad (1)$$

using linear regression. The analysis revealed a large coefficient of multiple determination ($R^2 = 0.941$), an indication of a high goodness-of-fit. Moreover, it showed (99.9% confidence level) that the probabilities that the values of A , a , b , c , and $\hat{E}_A$ were derived by chance alone (*i.e.*, that these values were actually are equal to zero) were $p < 1 \times 10^{-11}$ for all parameters, indicating that these were appropriately included in the model. (Values for the fitting parameters a , b , c , and $\hat{E}_A$, derived using linear regression, are within 10% of those obtained using ODR; the difference is attributable to the specified uncertainties in the T , P , and ϕ inputs, as well as differences between the fitting algorithms. Hence, we believe these fitting statistics to be relevant here.) Finally, we note that ignition delay time data can be scaled from one condition ($\tau_{ign}^{unscaled}$, $P^{unscaled}$, $\phi^{unscaled}$,

$C_n^{unscaled}, T)$ to another $(\tau_{ign}^{scaled}, P^{common}, \phi^{common}, C_n^{common}, T)$ according to Equation 2:

$$\tau_{ign}^{scaled} = \tau_{ign}^{unscaled} \left(\frac{P^{common}}{P^{unscaled}} \right)^a \left(\frac{\phi^{common}}{\phi^{unscaled}} \right)^b \left(\frac{C_n^{common}}{C_n^{unscaled}} \right)^c \quad (2)$$

4.2. Alternate correlations

We also experimented with a correlation that included a term for the degree of hydrogen unsaturation U_d . This parameter can be thought of as the number of C=C double bonds in the alkane-like carbon chain, where a fully saturated molecule has $U_d = 0$, and $U_d = 2$ corresponds to two degrees of unsaturation (*i.e.*, two double bonds in the carbon chain). This was incorporated by multiplying Equation 1 by the factor $(U_d + 1)^d$, where the exponent d was a fitting exponent parameter:

$$\tau_{ign} = AP^a \phi^b C_n^c (U_d + 1)^d \exp\left(\frac{\hat{E}_A}{\hat{R}_u T}\right) \quad (3)$$

The addition of unity to U_d was performed so that fully saturated molecules ($U_d = 0$) could be included in the linear regression. (A unity linear shift such as this has been recommended for use in logarithmic transformations [73, 74].) The logarithm of Equation 3 was analyzed using linear regression, revealing a p -value for the parameter d of $p = 0.105$. This indicates that for our data set this parameter was not significant even at the 90% level. By way of further confirmation, we applied the Akaike Information Criterion (AIC) with a likelihood-ratio test, with the result that the likelihood of information loss from a model that included U_d was not significantly lower than the likelihood of information loss from a model that did not include U_d [75]. Thus, we concluded that including fuel unsaturation was not necessary to capture the observed trends in the ignition data. Importantly, this seems to indicate that under the conditions studied, unsaturation has little effect on ignition delay times for large methyl esters.

Furthermore, it should be noted that the correlation introduced above assumes that the pressure, equivalence ratio, carbon number, and unsaturation scaling are not functions of temperature. In reality, the data show that at certain temperatures, the ignition delay time values for the FAMEs studied are *insensitive* to these parameters, or even that the scaling may reverse (negative instead of positive, *etc.*) [50, 51]. A third fitting equation that allowed parameters a , b , and c to vary as linear functions of temperature was also developed. The resulting correlation did not significantly improve the fitting results, and moreover was not warranted, given the uncertainty in the experimental data. Thus, while in principle a temperature-dependent scaling should be employed to summarize these data, such a regression has not been proposed here.

4.3. Oxygen mole fraction scaling

As mentioned earlier, several other studies have examined high-temperature ignition delay times of FAMES. In particular, Haylett, Davidson, and Hanson (2012) measured MD ignition times in 21%O₂/Ar mixtures [45], Li *et al.* (2012) and Wang and Oehlschlaeger (2012) measured MD ignition times in 21%O₂/N₂ mixtures [55, 56], and Wang, Gowdagiri, and Oehlschlaeger (2014) measured ignition times of MP, MO, and ML in 21%O₂/N₂ mixtures [58]. We have combined these data sets with our own ignition delay time results in order to derive oxygen mole fraction scaling parameters g for MD, MP, MO, and ML according to Equation 4:

$$\tau_{ign}^{scaled} = \tau_{ign}^{unscaled} \left(\frac{x_{O_2}^{common}}{x_{O_2}^{unscaled}} \right)^g \quad (4)$$

In order to obtain these parameters, we first scaled the data sets to common pressure and equivalence ratio values using published or conventional scaling values [51, 56, 58], then secondly fit the data using the logarithm-based approach outlined above (similar to Equation 1). The resulting oxygen mole fraction scaling parameters g are provided in Table 4. Note that these parameters are dependent on the pressure and equivalence ratio scaling exponents (a and b) used in the first step of this analysis, but in general a 10% change in these exponents (a or b) results in a change in the oxygen mole fraction scaling exponent g of 10% or less.

[Table 4 about here.]

5. Discussion

5.1. Graphical demonstration

The results of scaling the ignition delay times are best displayed graphically. Figure 2 shows the raw (unscaled) ignition delay times for MLA, MM, MP, MO, and ML, while Figure 3 shows the data scaled to $P^{common} = 6$ atm, $\phi^{common} = 1$, and $C_n^{common} = 16$ according to Equation 2 using the exponents given in Table 3. Notice that the correlation appropriately collapses the data to a general trend line, and that the error bars in the data points generally overlap this line. Both the graphical depiction and the statistical tests applied above serve to indicate the appropriateness of the equation and fitting parameters chosen. The residual range in the data points seen in the scaled plot (Figure 3) is due in part to the uncertainty in the original data and also in part to the temperature-dependent nature of the scaling parameters, as discussed in Section 4.2.

[Figure 2 about here.]

[Figure 3 about here.]

As seen in Figures 2 and 3, the different FAMEs examined in this study have very similar
150 ignition times; unscaled ignition delay times for different fuels differ by only about a factor
of 2-3 at any given temperature. The similarity in high-temperature ignition times for FAMEs
has been observed by others as well [58, 76–78], and has also been seen for other classes of
hydrocarbons [79, 80].

5.2. Experimental comparison

155 The parameters a , b , c , and $\hat{E}_A$ from Equation 1, and g from Equation 4, have important
physical significance and allow for quantitative comparisons of different fuels. Table 5 offers a
profile of different experimentally-determined scaling values for several classes of fuels, together
with those determined in this work. Several observations can be made based on this table.

[Table 5 about here.]

160 5.2.1. Pressure

In all cases shown in Table 5, the pressure scaling exponent a is negative. This reflects the
fact that collision rates increase with increasing pressure, thus decreasing the time necessary to
generate the critical radical concentration needed for an explosion. A similar pressure scaling can
be inferred using the Lindemann *et al.* mechanism for unimolecular decomposition reactions, as
165 pointed out by Imbert *et al.* [30, 81]. Returning to the pressure scaling values in Table 5, it is
important to note that not all fuels exhibit the commonly accepted $\tau \propto P^{-1}$ (*i.e.*, $a = -1$) scaling.
Use of this scaling is generally applicable, but in some cases can lead to significantly inaccurate
results.

5.2.2. Equivalence ratio

Table 5 also shows that the equivalence ratio-dependence of hydrocarbon ignition times
varies with oxygen concentration. At high x_{O_2} , the scaling parameter b is negative, whereas
at low x_{O_2} , b is positive. This change is found in some kinetic mechanisms as well. One such
mechanism is the Mehl *et al.* *n*-heptane model, which is a well-established tool for simulating
the combustion of this primary reference fuel and diesel surrogate [82, 83]. Figure 4 shows the

simulated equivalence ratio scaling exponent b at several oxygen mole fractions and four temperatures; notice, for instance, that at 1200 K, for $x_{O_2} > 0.2$ the model yields $b < 0$, whereas the opposite is true for lower oxygen mole fractions. We conducted an analysis to examine the sensitivity of the OH radical concentration [OH], a strong indicator of ignition at high temperatures, to the reaction rates of this n -heptane model. The modeling revealed that (at 1200 K and 7 atm) as x_{O_2} increased, the reactions

and

became significant ignition promoters, while the reaction

170 began to inhibit ignition. The precise coupling between the individual reaction rates and the equivalence ratio scaling is beyond the scope of this work. Nevertheless, the experimentally and computationally observed changes in the equivalence ratio scaling exponent b with x_{O_2} could have important implications for EGR in diesel engines, and thus should be studied further. Based on the above discussion, we note, in agreement with Horning *et al.* (2002), that scaling ignition
175 times over a large range of equivalence ratios is not advisable [27].

[Figure 4 about here.]

5.2.3. Carbon chain length

The carbon chain length scaling exponent c is seen to be negative in all cases, indicating that at high temperatures, ignition times tend to decrease as molecular size increases. Also,
180 a relatively close match is seen between the value measured by Horning, Davidson, and Hanson [27] ($c = -0.50$) and that of this study ($c = -0.61$). As pointed out by Davidson *et al.* [42], the increase in fuel reactivity with carbon chain length can be related to the decrease in average C–H bond strength (bond dissociation energy) with increasing carbon chain length. In particular, longer carbon chains have higher ratios of weaker secondary C–H bonds (C–C₂H₂) to stronger
185 primary C–H bonds (C–CH₃) [84–86]. Overall, however, it should be noted that differences between ignition times of large alkane-like fuels at high temperatures are expected to be relatively small [56, 79, 80].

5.3. Activation energy

Values for the activation energy $\hat{E}_A$ for the hydrocarbons listed in Table 5 range from about 25 to 51 kcal/mol, with most values near 45 kcal/mol. This parameter gives an indication of the sensitivity of the fuel's reactivity to temperature. It can also provide insight into the temperature-dependence of the unimolecular fuel decomposition pathways, as these have a large influence on high-temperature ignition times [50]. A larger activation energy indicates an increased sensitivity of the fuel's reactivity to temperature.

Close examination of the values in Table 5 seems to indicate a correlation between the oxygen mole fraction and the activation energy; in general, activation energy values seem to be greater than 40 kcal/mol for oxygen concentrations less than about 5%, and less than 30 kcal/mol for 21% oxygen mixtures. We employed the Mehl *et al.* *n*-heptane mechanism [82, 83] to examine this insight further at three pressures for stoichiometric argon-diluted mixtures, and the results are depicted in Figure 5. For all pressures shown, at oxygen contents greater than 21%, the activation energy is relatively insensitive to oxygen content. However, for oxygen contents less than 21%, the activation energy increases as the oxygen mole fraction decreases, and the effect is more pronounced at lower pressures as well. Importantly, this implies that high-temperature fuel ignition in diesel engines operating under oxygen-deprived EGR conditions is more temperature-sensitive, indicating that engine control may be more difficult.

[Figure 5 about here.]

Finally, we also note that the dependence of activation energy on oxygen content has implications for uncertainty quantification in shock tube ignition delay time measurements. Ignition time uncertainties are often derived from experimental temperature uncertainties using a simple Arrhenius equation:

$$\tau_{ign} = A \exp\left(\frac{\hat{E}_A}{\hat{R}_u T}\right) \quad (5)$$

$$\frac{\Delta\tau_{ign}}{\tau_{ign}} = \left(\frac{-E_A}{\hat{R}_u T}\right)\left(\frac{\Delta T}{T}\right) \quad (6)$$

Here, $\frac{\Delta\tau_{ign}}{\tau_{ign}}$ is the uncertainty in ignition time and $\frac{\Delta T}{T}$ is the uncertainty in the experimental temperature. Equation 6 implies that, all other factors held constant, ignition times measured in lower oxygen content mixtures may inherently have higher uncertainty because of the increased

210 activation energy values observed under these conditions. It should be noted, however, that work-
ing with dilute mixtures provides other benefits, such as minimal heat release and less violent
detonation events.

5.4. Oxygen mole fraction

The values for the oxygen mole fraction scaling exponent g for MD, MP, MO, and ML are
215 fairly similar to each other and to the values for n -alkanes obtained by Horning *et al.* (2002) [27]
and by Haylett *et al.* (2012) [45]. This points to the similarity of high-temperature ignition
processes between FAMES and normal alkanes. Also, like the pressure scaling exponents, all
oxygen mole fraction scaling exponents are negative. This reflects the fact that increased reactant
concentrations lead to higher collision rates, thereby promoting ignition.

220 5.5. Unsaturation

While this analysis did not reveal a significant hydrogen unsaturation U_d scaling exponent (d ;
see Section 4.2) for the FAMES studied, the data for MO and ML alone [50] may indicate that this
parameter nevertheless has some importance. In general, a positive unsaturation scaling ($d > 0$)
is predicted (increasing unsaturation leads to longer ignition times), which may be explained
225 by the fact that the double C=C bond in unsaturated FAMES changes the bond strength of the
neighboring C-H and C-C bonds [85, 87].

5.6. Graphical comparison

A graphical comparison of several ignition time correlations found in the literature with that
specified in this article is provided in Figure 6. These correlation trend lines were computed at
230 $P = 4$ atm, $\phi = 1$, $C_n = 8$, and $x_{O_2} = 0.04$. The correlations for n -alkanes [27, 42] predict
similar ignition times to those for the FAMES studied here, which is understandable given that
unimolecular decomposition of the alkane-like chain in FAMES governs biodiesel ignition times
at high temperatures [50]. Also, the trend line for i -octane correctly shows that it has much longer
ignition times than the n -alkanes and FAMES. Lastly, the activation energy (slope) of the FAME
235 trend line is lower than that of the other fuels shown (see also Table 5); this could be caused
in part by the temperature-dependent scaling that is characteristic of FAMES but less common
among n -alkanes [50, 51, 56].

[Figure 6 about here.]

5.7. Modeling comparison

240 It is also useful to compare experimentally-determined scaling parameters to those derived from chemical kinetic models [27, 30]. This can provide a quick benchmark for the accuracy of a model because the mechanism-derived scaling correlation parameter values are determined from numerous simulated conditions rather than just one set. In this work, we obtained ignition correlations from the Herbinet *et al.* (2011) [76], Westbrook *et al.* [50, 77, 78], and
245 Saggese *et al.* (2013) [88–90] biodiesel models by linear regression according to Equation 1 (see also Equation 1). Inputs to the linear regression algorithm were ignition times simulated in Chemkin Pro [91] using these models at T , P , ϕ , and C_n conditions (in 4%O₂/Ar mixtures) spanning the experimental conditions covered in Table 2 [50, 51]. The derived correlations are displayed graphically at $P = 6$ atm, $\phi = 1$, $C_n = 16$, and $x_{O_2} = 0.04$ in Figure 7, and the parameters for the trend lines are provided in Table 6. Note that since the Herbinet *et al.* model did not
250 include unsaturated species (*i.e.*, MO and ML), the correlation is only valid for $U_d = 0$. Also, since the Westbrook *et al.* and Saggese *et al.* biodiesel models only included molecules with $C_n = 16$ and $C_n = 18$, values for the carbon number scaling coefficient have not been provided (*i.e.*, $c = 0$)

255 [Figure 7 about here.]

[Table 6 about here.]

From Figure 7, it can be seen that the Herbinet model generally over-predicts FAME ignition times. Also, from Table 6, it appears that this model has an activation energy closer to most n -alkanes (see values listed in Table 5) rather than the FAMEs studied by Campbell *et al.* [50, 51].
260 Additionally, the Herbinet correlation shows a positive C_n scaling ($c > 0$), reflecting observations by Campbell *et al.* [51] that this model does not capture the effect of carbon chain length at present. In contrast, the Westbrook *et al.* [50, 77, 78] model, although not including a carbon number scaling parameter ($c = 0$), seems to produce a correlation that more closely approximates that obtained from the experimental data. Finally, the Saggese *et al.* [88–90] biodiesel model also
265 closely matches the experimental data correlation, but with a more accurate activation energy value.

6. Summary

We have examined the FAME ignition delay time data of Campbell *et al.* [50, 51] in order to determine a correlation that captures the pressure, equivalence ratio, and carbon chain length scaling of biodiesel surrogate ignition at low-oxygen-concentration conditions. The resulting correlation revealed negative pressure scaling, positive equivalence ratio scaling, and a negative carbon chain length dependence. Moreover, we have combined our experimental results with that of others [45, 55, 56, 58] in order to derive oxygen mole fraction scaling parameters for methyl decanoate, methyl palmitate, methyl oleate, and methyl linoleate, revealing negative scaling that is similar to that of normal alkanes. We have also provided comparisons of our correlation parameters to those derived for other classes of fuels, finding similar scaling parameters to those of *n*-alkanes but somewhat lower activation energy values. Finally, we obtained ignition correlations using the Herbinet *et al.* [76], Westbrook *et al.* [50, 77, 78], and Saggese *et al.* [88–90] biodiesel models, finding that the Herbinet model generally over-predicted ignition times and that the Westbrook and Saggese models had better accuracy. We believe that the correlations obtained in this work will be useful in developing EGR techniques for modern diesel engines, and will also aid in experimental designs for new biodiesel surrogate studies.

7. Acknowledgments

The measurement of ignition delay times of biodiesel surrogates was based upon work supported by, or in part by, the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grant number W911NF1310206. M.F.C. is supported by the Division of Chemical Sciences, Geosciences, and Biosciences, the Office of Basic Energy Sciences (BES), the U.S. Department of Energy (DOE). Also, during a portion of this work, M.F.C. was supported by a National Defense Science and Engineering Graduate (NDSEG) Fellowship, 32 CFR 168a. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. The authors would like to thank Kristen J. Campbell for useful insights and discussions concerning the statistical analysis.

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Table 1: Select high-temperature ignition time correlations found in the literature. Controls: τ_{ign} : ignition delay time; [brackets]: concentration; $\hat{R}_u$: ideal gas constant; P : pressure; T : temperature; ρ : density; ϕ : equivalence ratio. The activation energy values ($\hat{E}_A$ and B), the letter A , and the various lower-case letters ($a, b, \dots, n, m$) represent fitting parameters. Similar listings can be found in References [27, 29, 30].

Equation	Number	Fuel(s)	Reference
$\tau_{ign} = AP^a \phi^b C_n^c \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(7)	n -pentane, n -hexane, n -octane, and n -nonane	Davidson <i>et al.</i> (2010) [42]
$\tau_{ign} = AP^a \phi^b \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(8)	i -octane	Burwell and Olson (1965) [33]
$\tau_{ign} = A[\text{fuel}]^f [\text{O}_2]^g [\text{Ar}]^h \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(9)	Methane, propane, and n -heptane	Burcat <i>et al.</i> (1971, 1982) [34, 35, 37]
$\tau_{ign} = \left(\frac{P}{R_u T}\right)^a \exp\left(A + \frac{B}{T}\right)$	(10)	i -octane and n -heptane	Vermeer, Meyer, and Oppenheim (1972) [36]
$\tau_{ign} = AT^m [\text{fuel}]^f [\text{O}_2]^g [\text{Ar}]^h \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(11)	Ring-structured hydrocarbons	Burcat <i>et al.</i> (1979) [92]
$\tau_{ign} = A[\text{fuel}]^f [\text{O}_2]^g \rho^k \exp\left(\frac{B}{T}\right)$	(12)	Blends of primary reference fuels	Ryan and Callahan (1988) [38]
$\tau_{ign} = AP^a C_n^c \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(13)	Propane, n -butane, n -heptane, and n -decane	Horning, Davidson, and Hanson (2002) [27]
$\tau_{ign} = AP^a \phi^b \exp(n x_{\text{fuel}}) \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(14)	i -octane	Davidson <i>et al.</i> (2002) [39]
$\tau_{ign} = AP^a \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(15)	Cyclopentane and cyclohexane	Daley, Berkowitz, and Oehlschlaeger (2008) [40]
$\tau_{ign} = AP^a \phi^b T^m \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(16)	Number 2 diesel fuel (DF-2)	Haylett <i>et al.</i> (2009) [41]
$\tau_{ign} = A \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(17)	Hydrogen	Zhao, Chen, and Chen (2011) [43]
$\tau_{ign} = AP^a \phi^b \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(18)	n -decane, n -hexadecane, and methyl decanoate	Haylett, Davidson, and Hanson (2012) [45]
$\tau_{ign} = A[\text{fuel}]^f [\text{O}_2]^g \exp\left(\frac{\hat{E}_A}{R_u T}\right)$	(19)	n -nonane, methyl octanoate, and methylcyclohexane	Rotavera <i>et al.</i> (2011, 2013) [44, 46]

Table 2: Experimental conditions studied in References [50, 51] for MD, MLA, MM, MP, MO, and ML. Column headings: C_n : carbon chain length; U_d : degree of unsaturation; T : temperature; P : pressure; ϕ : equivalence ratio; x_{O_2} : oxygen mole fraction. All mixtures were diluted in argon. The combined data sets of the two studies contain 181 ignition delay time values.

Fuel	Formula	C_n	U_d	T [K]	P [atm]	ϕ	x_{O_2}	Ref.
MD	$C_{11}H_{22}O_2$	10	0	1026-1388	7	0.5	0.01, 0.21	[51]
MLA	$C_{13}H_{26}O_2$	12	0	1163-1354	3.5, 7	0.75, 1.25	0.04	[51]
MM	$C_{15}H_{30}O_2$	14	0	1162-1357	3.5, 7	0.75, 1.25	0.04	[51]
MP	$C_{17}H_{34}O_2$	16	0	1180-1311	3.5, 7	0.375, 0.75	0.04	[51]
MO	$C_{19}H_{36}O_2$	18	1	1115-1370	3.5, 7	0.75, 1.25, 2	0.04	[50]
ML	$C_{19}H_{34}O_2$	18	2	1128-1378	3.5, 7	0.75, 1.25, 2	0.04	[50]

Table 3: Best-fit parameters for Equation 1 based on MLA, MM, MP, MO, and ML ignition delay times at oxygen mole fraction $x_{\text{O}_2} = 0.04$ (diluted in argon; 166 data points). The $\pm$ numbers are standard error values for the fitting parameters.

Quantity	Value	Standard Error
A	2.24×10^{-6} ms	$\pm 0.71 \times 10^{-6}$ ms
a	-0.41	± 0.04
b	0.30	± 0.03
c	-0.61	± 0.08
$\hat{E}_A$	37.1 kcal/mol	± 0.7 kcal/mol
<i>Parameters</i>		
T range	1115-1378 K	
P range	3.2-7.3 atm	
ϕ range	0.27-2.39	
C_n range	12-18	
U_d range	0-2	
x_{O_2}	0.04	

Table 4: Oxygen mole fraction scaling parameters g for MD, MP, MO, and ML (see Equation 4). The $\pm$ numbers are standard error values for the fitting parameters, and the number of ignition delay time points used to derive each value are also given.

Fuel	x_{O_2} Exp. (g)	Standard Error	x_{O_2} Range	Number of Points
MD	-0.47	± 0.04	0.01-0.21	47
MP	-0.42	± 0.03	0.04-0.21	38
MO	-0.60	± 0.03	0.04-0.21	17
ML	-0.65	± 0.03	0.04-0.21	22

Table 5: Comparison of high-temperature ignition delay correlation parameters determined in this study (for MD, MLA, MM, MP, MO, and ML, according to Equations 1 and 4) and parameters from the literature (see Table 1). For uncertainties in the parameters from this study, see Tables 3 and 4. A similar table can be found in Imbert *et al.* [30].

Fuel(s)	P Range [atm]	x_{O_2} Range	P Exp. (a)	ϕ Exp. (b)	C_n Exp. (c)	x_{O_2} Exp. (g)	$\hat{E}_A$ [kcal/mol]	Refer
MLA, MM, MP, MO, and ML	3.2-7.3	0.04	-0.41	0.30	-0.61		37.1	This s
MD	6.4-50.5	0.01-0.21				-0.47		This s
MP	3.2-21	0.04-0.21				-0.42		This s
MO	6.5-10.9	0.04-0.21				-0.60		This s
ML	6.3-10.4	0.04-0.21				-0.65		This s
Methyl octanoate ($C_9H_{18}O_2$)	1-10	0.01	-0.19				48.7	[46]
MD	8	0.21	-1.32	-1.2			44.3	[45]
MD	13.7-18.5	0.21		-0.51			29.4	[56]
MD	7	0.21					25.9	[51]
MD	7	0.01					47.3	[51]
MP	10-20	0.21	-0.8	-0.5				[58]
n -alkanes C_3 , C_4 , C_7 , and C_{10}	1-6	0.02-0.20	-0.55		-0.50	-0.63	46.55	[27]
n -alkanes C_5 , C_6 , C_8 , and C_9	2	0.04	-0.53	0.80	-0.24		44.77	[42]
n -nonane (C_9H_{20})	1-10	0.01	-0.48				51.0	[46]
n -hexadecane ($C_{16}H_{34}$)	2-5	0.01-0.04	-0.73	0.82		-0.54		[45]
i -octane	1.2-8.2	0.005-0.06	-0.56	1.62			44.78	[39]
DF-2	2.3-8	0.21	-1.03	-1.02				[41]

Table 6: Best-fit parameters for Equation 1, derived by linear regression from the Herbinet *et al.* [76], Westbrook *et al.* [50, 77, 78], and Saggese *et al.* [88–90] biodiesel models. The best-fit values for the Herbinet model are based only on MLA, MM, and MP because it does not include unsaturated species (*e.g.*, MO and ML), and those for the Westbrook and Saggese models are based only on MP, MO, and ML because they do not include species smaller than MP (*i.e.*, MM and MLA). Standard error values for the fitting parameters derived in this study can be found in Table 3. Diluent is argon.

Quantity	This Study	Herbinet <i>et al.</i> (2011) [76]	Westbrook <i>et al.</i> (2011) [50, 77, 78]	Saggese <i>et al.</i> (2013) [88–90]
A	2.24×10^{-6} ms	3.54×10^{-8} ms	8.87×10^{-8} ms	7.14×10^{-7} ms
a	-0.41	-0.78	-0.46	-0.69
b	0.30	0.74	0.22	0.039
c	-0.61	0.072	[0]	[0]
$\hat{E}_A$	37.1 kcal/mol	46.7 kcal/mol	40.8 kcal/mol	37.3 kcal/mol
<i>Parameters</i>				
T range	1115-1378 K	1115-1378 K	1136-1333 K	1150-1375
P range	3.2-7.3 atm	3.5-7 atm	3.5-7 atm	3.5-7 atm
ϕ range	0.27-2.39	0.375-1.25	0.375-2	0.375-2
C_n range	12-18	12-16	16-18	16-18
U_d range	0-2	0	0-2	0-2
x_{O_2}	0.04	0.04	0.04	0.04