

Shelf-life of Biodiesel by Isothermal Oxidation Induction Period at Variable Temperatures

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Abstract

Biodiesel (fatty acid methyl esters [FAME]) is a renewable biomass-based diesel (BBD) fuel made from plant oils, animal fats and waste greases. Its production continues to increase globally, especially with more countries moving to increase the use of renewable fuels. One of the main disadvantages of biodiesel is its relatively poor oxidative stability. During longer periods of storage at fuel terminals or in vehicle tanks and fuel systems, biodiesel can react with oxygen in ambient air, leading to degradation that can adversely affect its viscosity and ignition quality. The shelf-life of biodiesel is an important property that can determine the conditions such as how long it can be stored at low temperatures. The objective of this work is to develop mathematical equations to estimating the shelf-life of biodiesel at $T = 25\text{ }^{\circ}\text{C}$. This was done by measuring the induction period by Rancimat instrument (IP_R) at different temperatures and extrapolating the results using two types of linear models. Model equations were developed from regression analysis performed on results for canola, palm and soybean oil-FAME (CaME, PME and SME), methyl oleate (MeC18:1) and methyl linoleate (MeC18:2). The best results from confirmation analysis were obtained for **Model B** type equations. This model type correlated $\ln(\text{IP}_R)$ with inverse T (T^{-1}) data and provided the most realistic estimates of the shelf-life (SL_B) of the five FAME studied in this work.

INTRODUCTION

Biodiesel, renewable diesel (“green” diesel) and sustainable aviation fuel (SAF) are three types of biomass-to-liquid fuels that can be made from vegetable oils, animal fats or waste cooking oils. Biomass-based diesel (BBD) such as biodiesel and renewable diesel are suitable for combustion in compression-ignition (diesel) engines. Production of these BBD has increased in the U.S. and throughout the world in recent years as efforts to develop renewable alternatives continue to be ramped up.

The Clean Fuels Alliance of America (CFAA) reported that 1.6 billion gal of total BBD were produced in the U.S. in 2022 (CFAA, 2022). This industry trade group has published its goal of ramping up production to 6 billion gal of BBD by 2030, a quantity that could eliminate 35 MMT of CO_2 -equivalent greenhouse gas emissions per year. As of January 2023, the U.S. Energy Information Administration estimated that biodiesel plant production capacity was 2.1 billion gal annually in the U.S. (EIA, 2023).

While renewable diesel may be used in blend ratios up to 100 vol%, this fuel is more expensive to produce than biodiesel (Lane, 2023). Production of renewable diesel is a multi-step continuous process that requires high-purity hydrogen gas, expensive metal catalysts, high pressures and temperatures and the liquid fuel needs to be separated by condensation from light fractions in the product stream (Gutiérrez-Antonio et al., 2015). In contrast, biodiesel is typically produced in one step under relatively mild conditions (ambient pressures and low temperatures [$\sim 60\text{ }^{\circ}\text{C}$]) and uses inexpensive base catalysts (Amin, 2019). Conversion time is relatively short (1-2 h) ameliorating the common use of batch or semi-batch process equipment.

The production of renewable diesel in the U.S. has increased significantly in the past five years. Partially as a result, increases in biodiesel production have slowed down. However, biodiesel is still relevant in many parts

of the world where refining capacity for renewable diesel production is limited or nonexistent. Countries such as Argentina, Brazil and Indonesia are continuing to increase their national production levels of biodiesel.

Currently, the ASTM fuel specification D6751 for biodiesel as a blending stock for mixing with conventional diesel fuel (petrodiesel) limits its content to 20 vol% ('B20') (ASTM, 2021). In recent years, governmental incentives favoring greener fuels as well as consumer demand have been the main driving forces for expanding biodiesel blend ratios in petrodiesel to 'B50' and higher. As a result, one of the major concerns with biodiesel, its relatively poor oxidative stability, is receiving increased attention.

When stored at the terminal or in fuel tanks and systems, biodiesel can be exposed to oxygen present in ambient air, making it susceptible to oxidative degradation, especially if it is exposed periodically to heat. Biodiesel is a fatty derivative that is primarily composed of alkyl esters of fatty acids obtained from the feedstock lipid. The most common form of biodiesel is fatty acid methyl esters (FAME). The FAME are composed of saturated, monounsaturated and polyunsaturated esters (SFAME, MUFAME and PUFAME). Reactivity of biodiesel with oxygen increases when its degree of unsaturation increases. While unsaturated FAME are significantly more reactive to oxygen than SFAME, linoleates are 40 times more reactive than oleates in neat systems without an added initiator (Frankel, 2005a).

Oxidative degradation can adversely affect the fuel quality of biodiesel by altering its kinematic viscosity (KV), acid value (AV) or peroxide value (PV). As a safeguard, the ASTM biodiesel fuel specification D6751 includes a minimum limit for oxidative stability as measured by induction period (IP) under accelerated conditions (ASTM, 2021). The IP is generally defined as the time period where the oxidation of biodiesel shifts from the formation of primary products (hydroperoxides) to the degradation of primary products to secondary products (acids, alcohols, aldehydes, ketones, lactones and aromatics) (Frankel, 2005a; Kamal-Eldin and Yanishlieva, 2005; White, 2000). Once this level of degradation is present, it is likely that its KV and AV increase above their respective maximum limits ($6.0 \text{ mm}^2 \text{ s}^{-1}$ at 40 degC and $0.50 \text{ mg KOH g}^{-1}$), diminishing the overall fuel quality.

When a Rancimat instrument is used to analyze oxidative stability, the result is term 'IP_R' (in h). According to ASTM specification D6751, this parameter is measured at $T = 110 \text{ degC}$ while the fuel sample is sealed in a test tube with 10 L h^{-1} air steadily bubbled through it (ASTM, 2021). If the sample yields $\text{IP}_R = 3 \text{ h}$ or longer, it is within specification, with respect to the oxidative stability. If not, then the biodiesel should be treated with antioxidants until it can pass the specification.

The IP_R is measured under tight laboratory conditions that include steadily bubbling the sample with air and an elevated measurement temperature 110 degC (ASTM, 2021). However, most realistic storage conditions will have lower temperatures, generally between 25 and 45 degC, and little if any constant contact with fresh air (oxygen). One common method used by the fats and oils industry is to measure IP_R data for the product at three or more temperatures and extrapolate the results to obtain "shelf-life" data at lower temperatures.

A simple formula used by the fats and oils industry to estimate the shelf-life of products is described by the **Model A** linear type equation (Dunn, 2008; Farhoosh, 2007; Frankel, 2005c; Nakatani et al., 2001):

$$\ln(\text{IP}_R) = A_0 + A_1(T) \quad (1)$$

where IP_R = induction period measured isothermally by a Rancimat instrument (in h), A_0 and A_1 are constants determined by linear regression analysis of $\ln(\text{IP}_R)$ versus T data and T = temperature (in K). For a given FAME mixture such as biodiesel, measuring IP_R for a series of elevated temperatures. Once the experimental data is analyzed to obtain coefficients A_0 and A_1 , then **Model A** type equations for a given FAME can be extrapolated to $T = 25 \text{ degC}$ (298.15 K) to calculate shelf-life (SL_A) as follows:

$$\ln(\text{SL}_A) = A_0 + A_1(298.15) \quad (2)$$

where SL_A is obtained by taking an inverse natural logarithm of the results from Eq. 2.

An alternative method for estimating the shelf-life of biodiesel and other fatty derivatives is to employ **Model B** type equations (Eq. 3) to extrapolate the results:

$$\ln(\text{IP}_R) = B_0 + B_1(T)^{-1} \quad (3)$$

where B_0 and B_1 are constants determined by linear regression analysis of $\ln(\text{IP}_R)$ versus T^{-1} data (Dunn, 2008). Analogous to **Model A** type equations, the IP_R of FAME are measured for a series of elevated temperatures, and the results analyzed to complete Eq. 3 and extrapolate it to calculate shelf-life (SL_B) at 25 degC (298.15 K) using the following equation:

$$\ln(\text{SL}_B) = B_0 + B_1(298.15)^{-1} \quad (4)$$

where SL_B is also obtained by taking an inverse natural logarithm of the outcome.

Another advantage of using the **Model B** approach is that it may be used to calculate the activation energy (E_a) and frequency factor (Z_0) for oxidation of biodiesel (Dunn, 2008). These parameters are useful in determining the reaction rate constant (k_T):

$$k_T = Z_0[\exp\{-E_a(R_g T)^{-1}\}] \quad (5)$$

where R_g = gas constant (8.3144 J mol⁻¹ K⁻¹). The E_a can be estimated from the following equation:

$$E_a = R_g(B_1) \quad (6)$$

where coefficient B_1 is defined in Eq. 3 and E_a is in kJ mol⁻¹.

The collision frequency factor can be estimated if the reaction kinetic model is known. For example, if the kinetics follow a first order model:

$$f(\alpha) = (1 - \alpha) \quad (7)$$

where α = degree of conversion, then Z_0 can be calculated as follows:

$$Z_0 = -\ln(1 - \alpha)[\exp\{-B_0\}] \quad (8)$$

Equation 8 can be generalized for different kinetic models by substituting $g(\alpha)$ for $-\ln(1 - \alpha)$ where $g(\alpha)$ is defined as:

$$g(\alpha) = [?]f(\alpha)^{-1}d\alpha \quad (9)$$

where the boundary limits 0 and α^* are defined as α at $t = 0$ and IP (Dunn, 2008; Khawam and Flanagan, 2006; Zhang et al., 2013).

The main objective of the present work is to develop model equations for estimating the shelf-life of biodiesel at $T = 25^\circ\text{C}$ (298.15 K) from the experimental IP_R - T data. Regression analyses were performed to obtain coefficients A_0 and A_1 in Eq. 1 for **Model A** type equations, and B_0 and B_1 in Eq. 3 for **Model B** type equations. One model equation of each type was developed for each of five FAME mixtures: canola, palm and soybean oil-FAME (CaME, PME and SME), methyl oleate (MeC18:1) and methyl linoleate (MeC18:2). Experimental IP_R data were measured at five temperatures for the first four FAME and at six temperatures for MeC18:2. Once the data were gathered and the **Model A** and **B** type correlations determined, the results were extrapolated according to Eqs. 2 and 4 to calculate SL_A and SL_B data for each FAME at 298.15 K. The final results were compared with each other and shelf-life data for biodiesel from the literature to assess how realistic the predictions from SL_A and SL_B were.

EXPERIMENTAL METHODS

Materials

Biodiesel samples were acquired from the following sources: 1) CaME was from Archer Daniels Midland (Decatur, IL, USA); 2) PME produced by Sime Darby Biodiesel Sdn. Bhd. (Selangor, Malaysia) with assistance from the Malaysian Palm Oil Board (Washington, DC, USA); and 3) SME was from Ag Environmental Products (Lenexa, KS, USA). According to the fuel producers, these biodiesel samples were not treated with performance enhancing additives including antioxidants. Fatty acid concentration profiles for these biodiesel fuels are presented in **Table S1** in the supporting information.

Pure MeC18:1 (99.5 ± 0.1 % 9(Z)-octadecenoic acid methyl ester) and MeC18:2 (99.0 ± 0.1 % 9(Z),12(Z)-octadecadienoic acid methyl ester) were supplied by Nu Chek Prep (Elysian, MN, USA). The purities of MeC18:1 and MeC18:2 were verified by analysis with a PerkinElmer (Waltham, MA, USA) Clarus 500 gas chromatograph (GC) with a flame ionization detector (FID) using an HP-88 column (30 m x 0.250 mm x 0.20 μ m) from Agilent (Santa Clara, CA, USA). The carrier gas was hydrogen and injector and detector temperatures were 240 °C and 280 °C. The temperature program was: 1) hold at 100 °C for 5 min; 2) ramp at 10 °C min⁻¹ to 220 degC; 3) hold at 220 degC for 15 min. Three replicate analyses were performed and results for the pure FAME were reported as average values.

Induction Period (IP_R)

A model 743 Rancimat instrument from Metrohm (Riverview, FL, USA) was employed to measure IP_R at five different temperatures for CaME, PME, SME and MeC18:1 and six temperatures for MeC18:2. Depending on the FAME, measurement temperatures ranged between 50 and 140 degC (323.15 and 313.15 K). The test method used to measure IP_R, EN 15751 (CEN, 2009), was conducted using the short-type test tubes on oil sample masses of 3 ± 0.1 g. Two replicate measurements were performed and the results reported as average values.

Mean absolute deviation (MAD) and root-mean-squared mean deviation (RMSD) data were calculated using the following two equations:

$$\text{MAD} = (\sum | \text{IP}_{R,i} - \text{IP}_i |) / n_i \quad (10)$$

$$\text{RMSD} = [(\sum (\text{IP}_{R,i} - \text{IP}_i)^2 / n_i)]^{1/2} \quad (11)$$

where IP_{R,i} = experimental IP_R value at temperature T_i, IP_i = IP value calculated from a model equation at T_i and n_i = total number of data pairs (IP_{R,i}, IP_i). The calculation of MAD and RMSD, least-squares linear regression analyses, analysis of variance (ANOVA) and statistical analysis operations were conducted in Microsoft (Redmond, WA, USA) Excel® spreadsheets.

RESULTS AND DISCUSSION

Composition and Fuel Properties

The fatty acid concentration profiles and fuel properties of CaME, PME and SME are summarized in **Tables S1** and **S2** in the supporting information. These results were discussed in full in an earlier study (Dunn, 2020) and a summary of those findings are presented herein.

Analysis of the FAME concentration profiles (**Table S1**) showed that the SME had a higher total PUFAME concentration (62.09 mass%) and a lower total MUFAME concentration (21.67 %) than either CaME (26.8 and 65.74 %) or PME (9.7 and 40.49 %). CaME had the lowest total SFAME concentration (7.40 %) followed by SME (16.21 %) and PME (49.82 %). SME had the highest calculated iodine value (IV) = 132.76 g I₂100⁻¹g⁻¹, followed by CaME (109.6) and PME (51.8).

Selected fuel properties of the three biodiesel fuels were summarized in **Table S2**. In descending order, IP_R at 110 degC was 9.34 h, 7.71 h and 2.745 h for CaME, PME and SME. The low value for SME was expected given its high total PUFAME content and comparable with data reported in other studies (Moser, 2008a, 2014, 2016; Yang et al., 2013). The experimental IP_R value for CaME was also comparable with data reported in the literature (Joshi et al., 2009; Moser, 2008b; Yang et al., 2013). However, the IP_R of PME was lower than that of CaME, despite PME having a lower total PUFAME concentration. Generally higher IP_R values (9.2-15.2 h) were reported for PME in the literature (Moser, 2008b, 2016; Sarin et al., 2010; Shahabuddin et al., 2012). In the earlier study (Dunn, 2020), it was postulated that PME had undergone partial degradation before its use in the study. PME had AV = 0.72 mg KOH g⁻¹ (**Table S2**), a value that exceeded the maximum limit (0.50 mg KOH g⁻¹) in the ASTM biodiesel fuel standard specification D6751 (ASTM, 2021). This higher value may have indicated that PME had undergone hydrolytic degradation. PME also exhibited a PV = 11.3 meq kg⁻¹ (**Table S2**), a value that was nearly twice the PV measured for CaME. Trace concentrations of hydroperoxides are known to act as autoxidation initiators (Frankel,

2005a; Kamal-Eldin and Yanishlieva, 2005). The effects of high AV and PV suggested that PME may have experienced autoxidation before being used in the study.

The pure MeC18:1 and MeC18:2 samples were also analyzed for IP_R . At 110 degC, $IP_R = 2.12 \pm 0.05$ h for MeC18:1, a value that was comparable with data reported in other studies (Knothe, 2008; Moser, 2009). Those studies also reported $IP_R = 0.94$ h and 1.0 h for MeC18:2. Nevertheless, no reliable IP_R data were obtained for MeC18:2 at 110degC in the present study.

IP_R Results at Variable Temperatures

Experimental IP_R data for the five FAME at variable temperatures are summarized in **Table 1**.

Also shown in the table are ‘Q10’ ratios and response factors (RF). These are defined as follows:

$$Q10 = (IP_R \text{ at } T) / (IP_R \text{ at } T + 10 \text{ degC}) \quad (12)$$

$$RF = (IP_R \text{ of FAME}) / (IP_R \text{ of MeC18:1}) \quad (13)$$

where T = temperature. The RF was calculated using IP_R data measured at the same T for the FAME and MeC18:1, which limited the results shown in the table to the range T = 90-130 degC for measuring the IP_R of MeC18:1.

Table 1 Oxidation induction period measured by Rancimat instrument (IP_R) of fatty acid methyl esters (FAME)

FAME	T	T	IP_R^a (h)	Q10 ^b	Q10 ^b	RF ^c
	°C	K		Ratio	Avg	
CaME	90	363.15	35.3 (0.3)			2.0
	100	373.15	16.0 (0.2)	2.2		2.00
	110	383.15	9.34 (0.04)	1.7		4.42
	120	393.15	4.41 (0.01)	2.12		5.3
	130	403.15	2.295 (0.007)	1.92	2.0	5.67
PME	100	373.15	16.5 (0.4)			2.1
	110	383.15	7.71 (0.06)	2.1		3.65
	120	393.15	3.57 (0.07)	2.16		4.3
	130	403.15	1.79 (0.08)	2.00		4.41
	140	413.15	0.88 (0.05)	2.04	2.1	
SME	80	353.15	32.8 (0.3)			
	90	363.15	14.34 (0.01)	2.3		0.8
	100	373.15	6.50 (0.01)	2.21		0.81
	110	383.15	2.745 (0.007)	2.37		1.3
	120	393.15	1.56 (0.02)	1.77	2.2	1.87
MeC18:1	90	363.15	17.78			1.0
	100	373.15	8.03 (0.04)	2.22		1.00
	110	383.15	2.11 (0.05)	3.79		1.00
	120	393.15	0.8 (0.1)	2.6		1.0
	130	403.15	0.40 (0.04)	2.0	2.7	1.00
MeC18:2	50	323.15	19.5			
	60	333.15	9.75 (0.09)	2.00		
	70	343.15	4.65 (0.04)	2.10		
	80	353.15	2.53 (0.01)	1.84		
	90	363.15	1.72 (0.04)	1.47		0.1
	100	373.15	1.03 (0.02)	1.68	1.82	0.13

T = Measurement temperature; CAME = canola oil-FAME; PME = palm oil-FAME; SME = soybean oil-FAME; Q10 = oxidation reactivity ratio; Avg = average value; RF = response factor.

^a Average values from $n = 2$ replicate measurements. Standard deviations (SD) in parentheses (blank if SD = 0).

^b Calculated from Eq. 12.

^c Calculated from Eq. 13.

The ‘Q10’ ratio is known as the relative oxidation reactivity for fatty derivatives (Frankel, 2005c; Ghosh et al., 2019; Pereira et al., 2015). For oxidation, this ratio is typically between 2 and 3, indicating that a 10 °C increase in T decreases IP_R by 50-66 %. Four FAME in **Table 1** exhibited average Q10 ratios of 2.0-2.7, while MeC18:2 had an average Q10 = 1.82, a value that was only 9.2 % below the lower threshold. An examination of the individual Q10 data for MeC18:2 shows that the ratio tended to decrease as T increased, with the Q10 < 2.00 occurring at higher temperatures. This may indicate that MeC18:2 was impacted by thermal decomposition as well as oxidative degradation at higher temperatures.

The IP_R of all five of the FAME studied could only be ranked at T = 100 °C. This ranking, in descending order was:

$$PME > CaME > MeC18:1 > SME > MeC18:2 \quad (14)$$

where the IP_R of PME was only slightly greater than that of CaME, with a probability (p) = 0.298 that the two values were equivalent. In general, when IP_R values were similarly ranked for two or more FAME (two FAME at 80 °C; four FAME at 90, 110 and 120 °C; three FAME at 130 °C), they followed this ranking. The only exception was observed for CaME and PME, where CaME had higher IP_R values at T = 110-130 °C. In this T-range, deviations between IP_R values for CaME and PME were significant (p [?] 0.012). It was noted earlier that analysis of the fuel properties of PME (**Table S1** in the supporting information) suggested the sample experienced a small degree of degradation before its use in the study. This is the most likely explanation for the otherwise unexpected observation that the IP_R of CaME was greater than that of PME, especially at T [?] 110 degC.

Model A

Plots of $\ln(IP_R)$ versus T representing **Model A** are presented in **Figure 1**. The straight lines drawn through the data verify the linear correlation between IP_R and T for the five FAME studied in the present work. Results from least squares regression analysis of the data are summarized in **Table 2**. These results yielded intercept and slope coefficients (A_0 and A_1) that were significant (p -value << 0.05). The A_0 coefficients for CaME, PME and SME were generally in a narrow range, from 28.1 to 31. The same trend was observed for the A_1 coefficients (-0.078 to -0.068) of these three FAME. In contrast, the A_0 and A_1 coefficients were significantly higher in magnitude for MeC18:1 (39 and -0.098) and lower in magnitude for MeC18:2 (22 and -0.059).

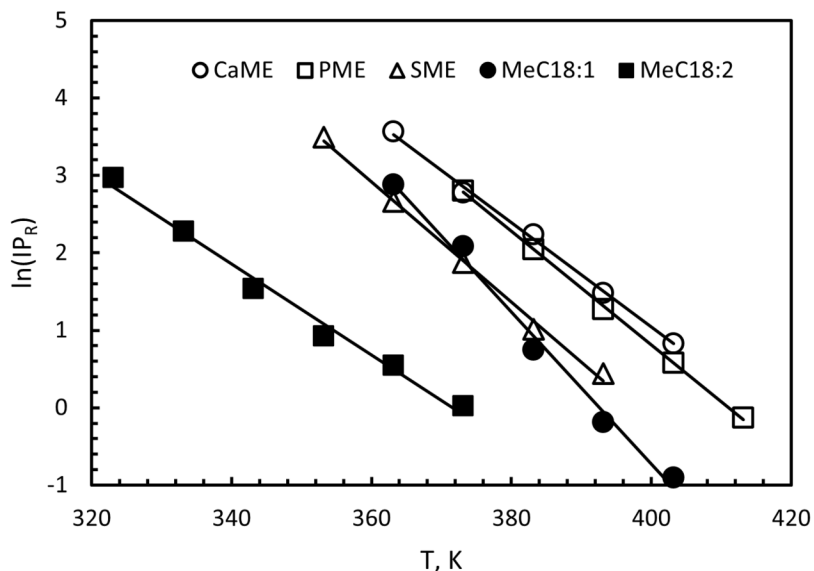


Fig. 1 Graph of $\ln(\text{IP}_R)$ as a function of T data for five fatty acid methyl ester (FAME) mixtures. IP_R = oxidative induction period measured by Rancimat instrument (h); T = temperature; CaME, PME and SME = canola, palm and soybean oil-FAME; MeC18:1 = methyl oleate (99.5 %); MeC18:2 = methyl linoleate (99.0 %). Lines drawn through the data points represent results from linear regression analyses according to **Model A**.

The linear correlation from application of **Model A** to IP_R - T data was well established, with respect to correlation coefficients (R^2) [?] 0.985. The results also exhibited low standard

Table 2 Results from regression analysis of $\ln(\text{IP}_R)$ versus T data (**Model A**). $\ln(\text{IP}_R) = A_0 + A_1(T)$; IP_R in h, T in K

Parameter	CaME	PME	SME	MeC18:1	MeC18:2
df	3	3	3	3	4
A_0	28.1	30.2	31	39	22
$\text{Err}[A_0]$	0.7	0.4	1	2	1
p -value	0.00004	0.000004	0.00009	0.0004	0.00004
A_1	-0.068	-0.0734	-0.078	-0.098	-0.059
$\text{Err}[A_1]$	0.002	0.0005	0.003	0.006	0.003
p -value	0.00005	0.000005	0.0001	0.0004	0.00005
R^2	0.997	0.9993	0.995	0.987	0.985
σ_y	0.06	0.03	0.09	0.2	0.1
F-ratio	1,242	6,049	750	299	328

df = Degrees of freedom; A_0 = intercept coefficient; A_1 = slope coefficient; $\text{Err}[A_i]$ = standard error of coefficient ' A_i '; p -value = probability A_i [?] 0 (< 0.05); R^2 = adjusted correlation coefficient; σ_y = standard error of the y-estimate; F-ratio = variance ratio (model/residuals). See **Table 1** for abbreviations.

errors of the y-estimate (σ_y [?] 0.2) for calculating $\ln(\text{IP}_R)$ directly from T data. Results from ANOVA demonstrated high variance (F-) ratios (model/residuals), indicating that the goodness

of fit of the model equations was high. However, examination of the data in **Figure 1** revealed small degrees of curvature in the data for MeC18:2. **Figure S1** is a residual plot in the supporting information (residuals = $IP_R - IP_A$ [IP calculated from the corresponding **Model A** equation]) that revealed a non-random pattern, suggesting that a linear model may be insufficient for correlating IP_R to T. When the data for MeC18:2 were fitted to a second-order polynomial by regression analysis, the results showed that R^2 increased from 0.985 to 0.997 and F-ratio from 328 to 850 relative to the linear model summarized in **Table 2**. All three regression coefficients had p -value [?] 0.02 and σ_y decreased from 0.1 to 0.06. Nevertheless, it was desired to maintain consistency in the application of **Model A** to correlate IP_R -T data for the five FAME studied herein. Therefore, the linear model equations summarized in **Table 2** were employed to calculate shelf-life data at 25 °C for all FAME, including MeC18:2.

Shown in **Figure 2** is a confirmation graph of IP_A values *versus* experimental IP_R values. The dashed line drawn through the data represents the $IP_A = IP_R$ line. All data points appear in

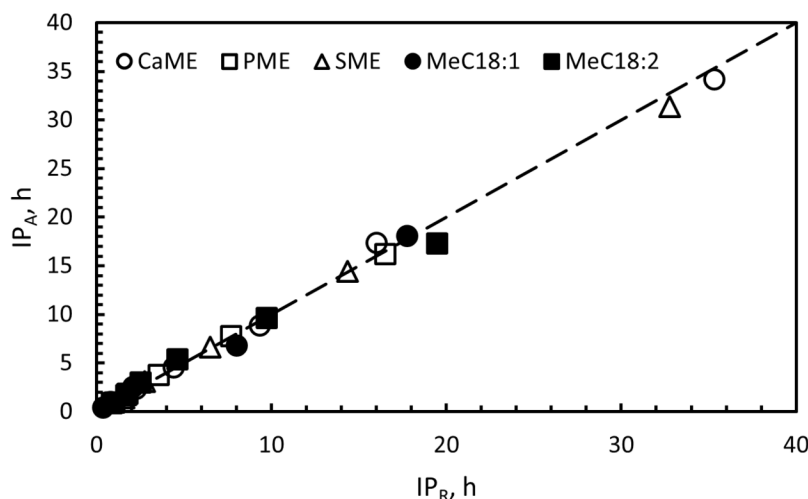


Fig. 2 Confirmation analysis of IP data calculated from **Model A** equations (IP_A) *versus* experimental IP_R data. Dashed line: $IP_A = IP_R$. See **Fig. 1** for abbreviations

close proximity to the dashed line, suggesting the application of **Model A** yielded good results for all five FAME. Consequently, regression analysis of the data in **Figure 2** yielded linear

correlations (R^2 [?] 0.989) between IP_A and IP_R , (**Table 3**). These results yielded intercept coefficients (C_0) that were low in value, between -0.1 and +0.6 and ANOVA yielded p -value > 0.05, suggesting that a value of zero (0) can be assumed for C_0 . On the other hand, the slope

Table 3 Results from confirmation analysis of IP calculated from **Model A** equations (IP_A) *versus* experimental IP_R data. $IP_A = C_0 + C_1(IP_R)$

Parameter	CaME	PME	SME	MeC18:1	MeC18:2
df	3	3	3	3	4
C_0	0.3	0.11	0.4	-0.1	0.6
Err[C_0]	0.6	0.09	0.2	0.5	0.3
p -value	0.6	0.3	0.2	0.9	0.2
C_1	0.97	0.97	0.95	0.99	0.87
Err[C_1]	0.04	0.01	0.01	0.05	0.04

Parameter	CaME	PME	SME	MeC18:1	MeC18:2
p -value	0.0001	0.000003	0.000008	0.0003	0.00002
R^2	0.994	0.9996	0.9990	0.989	0.991
σ_y	1	0.1	0.4	0.8	0.6
F-ratio	710	8,904	4,136	353	552
MAD ^a	0.63	0.12	0.43	0.42	0.62
RMSD ^b	0.84	0.19	0.66	0.62	0.98

C_0 = Intercept coefficient; C_1 = slope coefficient; $\text{Err}[C_i]$ = standard error of coefficient ' C_i '; p -value = probability $C_i \neq 0$ (< 0.05); MAD = mean absolute deviation; RMSD = root-mean-squared deviation. See **Table 1** and **2** for abbreviations.

^a Deviations between IP_R and IP_A ; calculated from Eq. 10.

^b Deviations between IP_R and IP_A ; calculated from Eq. 11.

coefficients (C_1) were significant with values for four of the FAME being in the range 0.95-0.99, which was close to the desired value of unity (1) for a model confirmation analysis. The results

for MeC18:2 yielded a lower C_1 coefficient (0.87), suggesting that its model equation under predicted IP_A , with respect to its corresponding experimental IP_R values. This was confirmed for four of the six data pairs evaluated for MeC18:2, specifically the IP_R data at $T = 50, 60, 90$ and 100°C (323.15, 333.15, 363.15 and 373.15 K).

The MAD and RMSD results obtained from application of Eqs. 10 and 11 to (IP_R, IP_A) data pairs are summarized in **Table 3**. These data showed generally low values where $\text{MAD} = 0.12\text{-}0.63$ and $\text{RMSD} = 0.19\text{-}0.98$. MeC18:2 had the highest RMSD value, a result that may have been influenced by the relatively low C_1 coefficient in its model confirmation equation. On the other hand, CaME yielded the highest MAD value (0.63), despite having a relatively high C_1 coefficient (0.99) while the MAD value of MeC18:2 was slightly lower.

The residuals ($IP_R - IP_A$) calculated from applying the **Model A** type equations for the five FAME are presented in **Figure 3**. In general, the residuals were ≈ 0.51 for 20 of the 26 total data pairs. Of the remaining six data pairs, only one residual exceeded 1.43, which was for

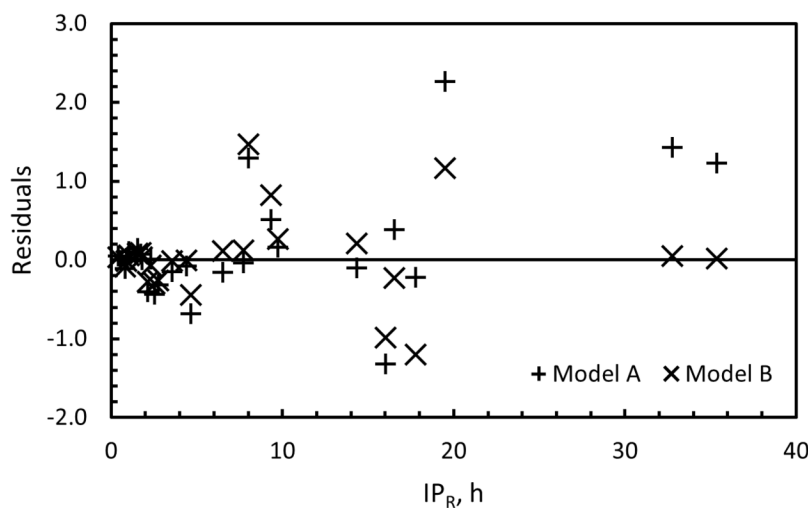


Fig. 3 Residual data from application of **Models A** and **B** equations versus experimental data. Residual = $IP_R - [IP_A \text{ or value calculated from Model B } (IP_B)]$. See **Figs. 1** and **2** for abbreviations

MeC18:2 at $T = 50^\circ\text{C}$ (323.15 K; residual = 2.26). In summary, it appears that the application of **Model A** to IP_R - T data did a good job in predicting IP_A values within the range of measurement temperatures for all five of the FAME studied in the present work.

Model B

Experimental results plotted as $\ln(IP_R)$ versus T^{-1} curves for **Model B** are shown in **Figure 4**. The lines drawn through the data demonstrate a linear correlation (R^2 [?] 0.989) between IP_R and T^{-1} for all five FAME, an observation that is verified in the regression analysis results presented in **Table 4**. The intercept and slope coefficients for **Model B** (B_0 and B_1) were significant (p -

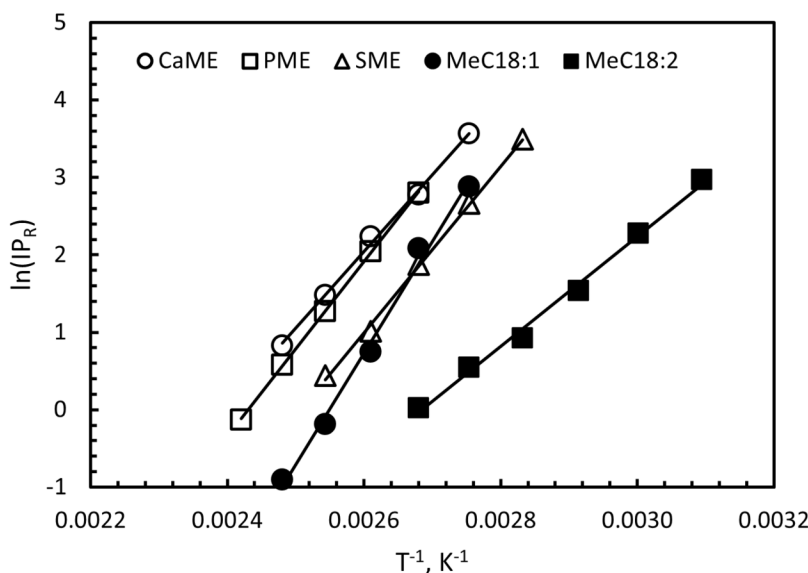


Fig. 4 Graph of $\ln(IP_R [h])$ as a function of T^{-1} data for CaME, PME, SME, MeC18:1 and MeC18:2. Lines drawn through the data points represent results from linear regression analyses according to **Model B**. See **Fig. 1** for abbreviations

value $\ll 0.05$). Similar to the results for **Model A**, the intercept and slope coefficients for CaME, PME and SME were in narrow ranges, between -27.5 and -23.7 for B_0 , and between 9,900 and 11,320 for B_1 . Also correspondingly, the B_0 and B_1 coefficients were significantly higher in magnitude for MeC18:1 (-37 and 14,400) and lower in magnitude for MeC18:2 (-19.1 and 7,100).

Table 4 Results from regression analysis of $\ln(IP_R)$ versus T^{-1} data (**Model B**). $\ln(IP_R) = B_0 + B_1(T^{-1})$; IP_R in h, T in K

Parameter	CaME	PME	SME	MeC18:1	MeC18:2
df	3	3	3	3	4
B_0	-23.7	-27.5	-27.0	-37	-19.1
Err[B_0]	0.8	0.2	0.7	2	0.7
p -value	0.00008	0.000001	0.00005	0.0003	0.00001
B_1	9,900	11,320	10,800	14,400	7,100

Parameter	CaME	PME	SME	MeC18:1	MeC18:2
Err[B ₁]	300	90	300	800	300
<i>p</i> -value	0.00006	0.000001	0.00004	0.0003	0.00001
R ²	0.996	0.9998	0.997	0.989	0.993
σ _y	0.07	0.02	0.06	0.2	0.09
F-ratio	1,059	16,019	1,518	368	750

B₀ = intercept coefficient; B₁ = slope coefficient; Err[B_i] = standard error of coefficient ‘B_i’; *p* -value = probability B_i [?] 0 (< 0.05). See **Tables 1** and **2** for abbreviations.

The linear correlations obtained from application of **Model B** to IP_R-T⁻¹ demonstrated in the high R² coefficients, low σ_y ([?] 0.2) and high F-ratios ([?] 368), all indicators that the model equations had relatively high goodness of fit for each FAME. Similar to the results from applying **Model A**, the **Model B** results for MeC18:2 in **Figure 4** exhibited some curvature in the data. The residual plot for MeC18:2 (see **Figure S2** in the supporting information) revealed a non-random pattern and fitting the data to a second-order polynomial (data not shown) resulted in slight improvements for R² (0.997), F-ratio (848) and σ_y (0.06). However, the three regression coefficients had *p* -value [?] 0.09, indicating they were not significant to the correlation of the data. Given these results, the linear model described by **Model B** was determined to be sufficient for correlating IP_R-T⁻¹ data for MeC18:2. Therefore, the linear correlation results in **Table 4** were employed to calculate shelf-life results at 25 °C for all FAME studied in the present work.

A conformation graph showing IP_B data calculated from application of the **Model B** equations *versus* experimental IP_R data is presented **Figure 5**. Analogous to the results in **Figure 2**, all data points are in close proximity to the dashed line representing IP_B = IP_R. This suggested

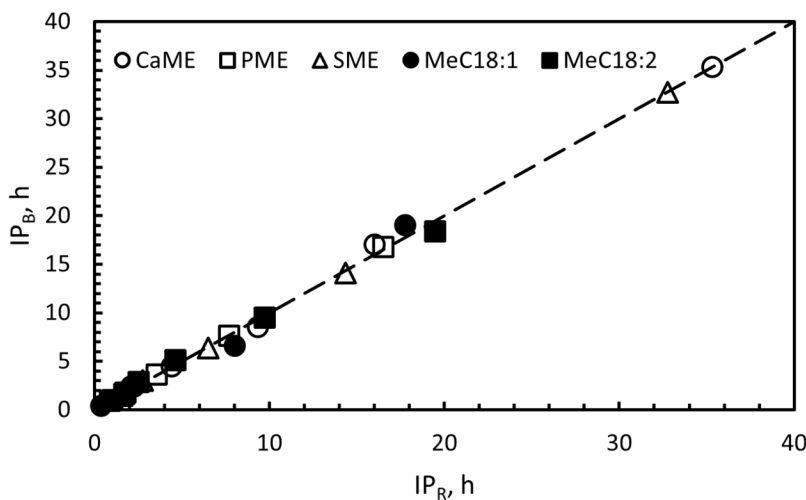


Fig. 5 Confirmation analysis of IP_B data calculated from **Model B** equations *versus* experimental IP_R data. Dashed line: IP_B = IP_R. See **Figs. 1** and **3** for abbreviations

that the application of **Model B** yielded good results for all five FAME studied in the present work. Results from regression analysis of the data in **Figure 5** are summarized in **Table 5**. These analyses yielded linear correlations (R² [?] 0.982) between IP_B and IP_R. The intercept

Table 5. Results from confirmation analysis of IP calculated from **Model B** equations (IP_B) *versus* experimental IP_R data. IP_B = D₀ + D₁(IP_R)

Parameter	CaME	PME	SME	MeC18:1	MeC18:2
df	3	3	3	3	4
D_0	0.0	-0.06	0.0	-0.3	0.3
Err[D_0]	0.5	0.07	0.1	0.6	0.2
p -value	0.9	0.4	0.98	0.7	0.2
C_1	1.01	1.014	0.996	1.05	0.93
Err[D_1]	0.03	0.008	0.008	0.07	0.02
p -value	0.00004	0.000001	0.000001	0.0007	0.000001
R^2	0.997	0.9997	0.9998	0.982	0.998
σ_y	0.7	0.1	0.2	1	0.3
F-ratio	1,338	14,165	16,772	218	2,028
MAD	0.38	0.081	0.14	0.61	0.39
RMSD	0.57	0.12	0.16	0.86	0.54

D_0 = Intercept coefficient; D_1 = slope coefficient; Err[D_i] = standard error of coefficient ' D_i '; p -value = probability D_i [?] 0 (< 0.05). See **Tables 1-3** for abbreviations.

coefficients (D_0) that were very low (between -0.3 and +0.3) and ANOVA indicated they were not significant (p -value > 0.05) allowing $D_0 = 0$ to be assumed. The slope coefficients (D_1) were significant (p -value $<< 0.05$) with values for four of the FAME being close to unity (0.996-1.05) indicating good confirmation of these model equations. Similar to the results for **Model A**, the **Model B** confirmation equation for MeC18:2 yielded the lowest D_1 coefficient (0.93), suggesting that its model equation under predicted IP_B , with respect to experimental IP_R values. This was confirmed for four of the six data pairs evaluated for MeC18:2, where $IP_R > IP_B$ at the same four temperatures (50, 60, 90 and 100 °C [323.15, 333.15, 363.15 and 373.15 K]) as observed above for its **Model A** equation.

The MAD and RMSD results calculated from (IP_R , IP_B) data pairs are presented in **Table 5**. Similar to the results for **Model A**, the confirmation results for **Model B** exhibited generally low values, MAD = 0.081-0.61 and RMSD = 0.12-0.86. MeC18:2 had the highest MAD and RMSD values, suggesting its predicted IP_B values were influenced by the lower D_1 coefficient in its confirmation equation.

The results for the residuals ($IP_R - IP_B$) calculated from application of the **Model B** type equations to the data for the five FAME are presented in **Figure 3**. Overlaid with these results are residuals ($IP_R - IP_A$) obtained from the **Model A** equations (discussed earlier). In general, the residuals for **Model B** were [?] 1.47 for all 26 data pairs with 21 data pairs having residuals [?] 0.44. The highest residual (1.47) was for MeC18:1 at $T = 100$ degC (373.15 K). Summarizing the **Model B** results, the application of this type of model equation to $IP_R - T^{-1}$ data did an excellent job predicting IP_B values within the range of measurement temperatures corresponding to the five FAME studied in the present work.

Direct comparison of results from applying **Model A** and **Model B** type equations to IP_R data for the five FAME showed that the calculation of IP_B values from the **Model B** equations yielded more accurate results. This is best demonstrated by the deviation results obtained from confirmation analyses performed on both models. First, comparing the data plotted in **Figures 2** and **5** shows that IP_A data points tended to be more separated from the dashed line than the IP_B results, especially when $IP_R > 15$ h. This observation is supported by the residuals data overlaid for **Models A** and **B** in **Figure 3**. These results demonstrate that residuals were generally larger in the IP_A data than the IP_B data. Finally, comparing MAD and RMSD data in **Tables 3** and **5** shows that values were consistently lower for **Model B** results for four of the five FAME studied herein. The exception was observed for MeC18:1, where the **Model A** results yielded MAD = 0.42 and RMSD = 0.62, values that were slightly lower than those for the **Model B** results (0.61 and 0.86).

Shelf-life Results from Extrapolation of Models A and B Equations

Thermal degradation at temperatures above 60 degC can alter the mechanism of oxidation due to the solubility of oxygen decreasing as temperature increases (Frankel, 2005b). Measurement of the IP_R works by the evolution of volatile organic acids from the heated oil which can be swept by the continuous flow or air into a test tube containing deionized water (Frankel, 2005c). The water-organic acid mixture is continuously monitored by a conductivity probe and increases are recorded as a function of time. The IP_R is then calculated at the onset point where conductivity increases exponentially. Decreasing the measurement temperature hinders the formation of volatile organic acids. Therefore, elevated temperatures (60-140 degC) are necessary to generate them for the analysis of IP_R . This condition is the main driving force for estimating the shelf-life of fatty derivatives such as biodiesel by extrapolating IP_R -T data to lower temperatures.

Model A and **Model B** type equations obtained for the five FAME studied herein were extrapolated to estimate shelf-life data at $T = 25$ degC (298.15 K). These results are summarized under columns showing calculated data for **Model A** (SL_A) and **Model B** (SL_B) in **Tables 6** and **7**. The general procedure for both model types was to first calculate $\ln(IP_A)$ or $\ln(IP_B)$ using either Eq. 2 or Eq. 4, then take the inverse natural logarithm to obtain the SL_A or SL_B results for each FAME. Also presented in the tables are confidence intervals calculated at 95 % confidence levels.

Table 6 Shelf-life of FAME at $T = 25$ degC (298.15 K) calculated from **Model A** type equations (SL_A)

FAME	SL_A^a (h)	Confidence Limits ^b	
		Upper	Lower
CaME	2,760	3,190	2,390
PME	3,970	4,250	3,700
SME	2,220	2,750	1,800
MeC18:1	10,700	16,400	7,000
MeC18:2	74.8	99.8	56.0

See **Tables 1-3** for abbreviations.

^a Procedure for each FAME: 1) calculate $\ln(IP_A) = A_0 + A_1(298.15 \text{ K})$ [A_0 and A_1 from **Table 2**]; 2) SL_A = inverse natural log of extrapolated $\ln(IP_A)$ value.

^b Confidence level = 95 %.

Table 7 Shelf-life of FAME at $T = 25$ °C (298.15 K) calculated from **Model B** type equations (SL_B)

FAME	SL_B^a (h)	Confidence Limits ^b	
		Upper	Lower
CaME	13,400	15,700	11,500
PME	34,400	36,000	33,000
SME	9,080	10,500	7,830
MeC18:1	108,000	159,000	74,000
MeC18:2	116	140	95.5

See **Tables 1**, **4** and **5** for abbreviations.

^a Procedure for each FAME: 1) calculate $\ln(IP_B) = B_0 + B_1(298.15 \text{ K})$ [B_0 and B_1 from **Table 4**]; 2) SL_B = inverse natural log of extrapolated $\ln(IP_B)$ value.

^b Confidence level = 95 %.

The SL_B data for CaME, PME and MeC18:1 were an order in magnitude greater than the corresponding

SL_A data. For these three FAME, the SL_B values were 4.9, 8.7 and 10.0 times higher than the respective SL_A values. The SL_B of SME was 4.1 times greater than its SL_A , while the SL_B for MeC18:2 was only 55 % higher than its SL_A . It appears the inflation in the SL_B values relative to corresponding SL_A values was larger for the three FAME with high total MUFAME concentrations ([?] 40.49 mass%). In contrast, FAME with high total PUFAME concentrations (62.09 % for SME and 99.0 % for MeC18:2) exhibited smaller increases in SL_B , with respect to SL_A . Nevertheless, SL_B was consistently greater than SL_A for all five FAME studied in the present work.

A comparison of SL_A results with shelf-life data reported in two earlier studies is presented in **Figure 6**. The results presented in the present work compared well with the ‘SL(1)’ data reported in an earlier study (Dunn, 2020). In that study, shelf-life data were obtained by

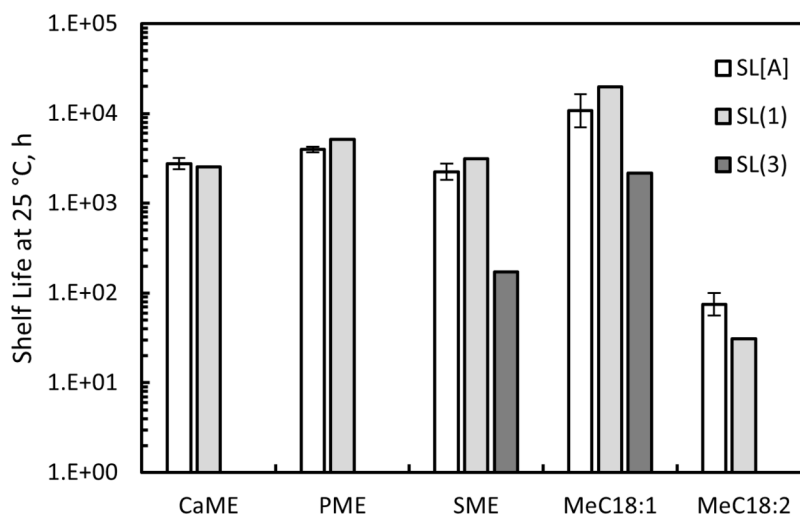


Fig. 6 Comparison of shelf-life data (SL_A) data obtained from extrapolation of the **Model A** type equations to 25 °C (298.15 K) with shelf-life data [$SL(1)$ and $SL(3)$] reported in earlier studies (Dunn, 2008, 2020). Error bars for SL_A data are 95 % confidence intervals taken from **Table 6**. See **Fig. 1** for abbreviations

linear regression of IP_R -T data and extrapolating the resulting equations to $T = 25$ °C. However, the $SL(1)$ data were obtained from equations derived from experiments performed at three temperatures in the ranges $T = 90$ -110 °C (363.15-383.15 K) for CaME, PME, SME and $T = 80$ -100 °C (353.15-373.15 K) for MeC18:2. In the present work, SL_A data were calculated from **Model A** type equations derived from analysis of IP_R -T data measured at five or six measurement temperatures. As a consequence, variations between SL_A and $SL(1)$ data from the earlier study were observed. While $SL_A > SL(1)$ for CaME and MeC18:2, the opposite trend was noted for PME, SME and MeC18:1. In the cases where $SL_A > SL(1)$, deviations were small, 200 h for CaME and 44 h for MeC18:2. In the remaining three cases, deviations were larger with MeC18:1 demonstrating the largest deviation (9,000 h), followed by PME (1,200 h) and SME (900 h).

Ranking the calculated SL_A results in descending order yielded the following:

MeC18:1 > PME > CaME > SME > MeC18:2 (15)

This order generally agrees well with what would be expected based on the degrees of unsaturation (DU) of PME, CaME, SME and MeC18:2, where $DU = 0.58, 1.28, 1.53$ and 2.00 (calculated from results in **Table S1** in the supporting information). Predicting the shelf-life of FAME generally does not correlate well with DU (Knothe, 2002) and this is exemplified when considering that according to SL_A , MeC18:1 held the highest ranking above despite having $DU = 1.00$, a value that was greater than the DU calculated for

PME. Nevertheless, ranking the SL(1) data reported earlier (Dunn, 2020) yielded similar results with the remarkable exception that CaME [SL(1) = 2,560 h] and SME (3,130 h) were switched in the rankings. The ranking from the earlier work was curious since SME had a significantly higher total PUFAME concentration (62.09 mass%) than CaME (26.77 %). Given the aforementioned differences in the experimental method for acquiring and analyzing IP_R-T data to estimate SL_A for the present work and SL(1) in the earlier study, the change in the ranking of CaME and SME suggests that the methodology can significantly impact the outcomes of the analyses. Therefore, it was concluded that the method employed in the present work (five to six IP_R-T data points over variable T-ranges) yielded more reliable results than the method used in the earlier study, with respect to the estimation of the shelf life of biodiesel at lower temperatures.

Two data points in **Figure 6** were represented as ‘SL(3)’ results reported in an earlier study (Dunn, 2008). This study was carried out using a different instrument to measure the IP, which was generally termed as the oil stability index (OSI). The experimental data were measured taken at six temperatures in the range T = 60-80 °C (333.15-353.15 K) for SME and eight temperatures in the range T = 60-95 °C (333.15-368.15 K) for MeC18:1. The SL_A values for SME and MeC18:1 were 12.9 and 5.0 times greater than their corresponding SL(3) values. The most likely explanation for these poor comparisons was the variation in instruments and experimental conditions employed to measure the respective IP data for analysis.

The SL_B data obtained from extrapolation of the **Model B** equations are presented graphically in **Figure 7**. These data are presented in a separate figure mainly for convenience

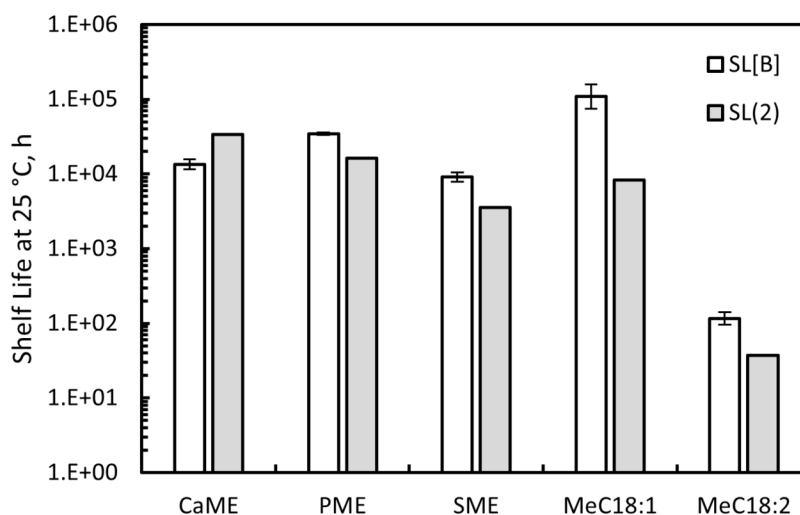


Fig. 7 Comparison of shelf-life data (SL_B) data obtained from extrapolation of the **Model B** type equations to 25 °C (298.15 K) with shelf-life data [SL(2)] reported in an earlier study (Dunn, 2020). Error bars for SL_B data are 95 % confidence intervals taken from **Table 7**. See **Fig. 1** for abbreviations

and to avoid overcrowding the results presented in **Figure 6**. Presented alongside the SL_B data are shelf-life data obtained from analysis of pressurized-differential scanning calorimetry (P-DSC) data reported in an earlier study (Dunn, 2020), which are denoted as ‘SL(2)’. The mathematical procedures for estimating the SL(2) data are explained in more detail in the earlier work.

The SL_A and SL(2) data were most comparable for SME, MeC18:1 and MeC18:2, where the deviations were -1,400, 2,400 and 37 h, respectively. On the other hand, deviations for CaME and PME were much larger (-31,100 and -12,200 h). Similar comparison of SL_B and SL(2) data suggested that the values may be comparable for MeC18:2 (deviation = 78 h). Otherwise, the deviations for CaME, PME, SME and MeC18:1 were larger (-20,500, 18,200, 5,500 and 99,700 h). Analogous results were observed from comparison of SL_B

and SL(1) results, where deviations for MeC18:2 were lowest (85 h), while those for CaME, PME, SME and MeC18:1 were larger (10,800, 29,200, 5,950 and 88,300 h).

Ranking the SL_B values in **Table 7** in descending order yielded the following results:

$$MeC18:1 > PME > CaME > SME > MeC18:2 \quad (16)$$

This ranking was identical to the ranking shown noted in Eq. 15 for SL_A . The calculated SL_B of MeC18:1 was between one and two orders in magnitude greater than the SL_B values for CaME, PME and SME, and three orders in magnitude greater than the SL_B of MeC18:2. Compared with the SL_A and SL_B rankings in the present work, the SL(2) data reported in (Dunn, 2020) exhibited some variations, where CaME had the highest value, followed by PME, MeC18:1, SME and MeC18:2. This ranking did not agree well with those shown in Eqs. 15 and 16 for SL_A and SL_B . It is possible that thermal degradation occurred in the non-isothermal P-DSC scans conducted for the earlier study (Dunn, 2020). These effects may have altered the reaction kinetics as the P-DSC cell temperature was ramped to higher temperatures.

Earlier, it was noted that SL_B was consistently greater than SL_A for all five FAME studied in the present work. For CaME, PME and MeC18:1, deviations between these two values were more than one order in magnitude. There may be some question on the reliability of SL_A and/or SL_B data as estimates for the shelf-life of biodiesel at low temperatures. For example, $SL_A = 2,760$ h and $SL_B = 13,400$ h were estimated for CaME (see **Tables 6** and **7**). These data convert to 115 d (16.4 wk) and 558 d (79.8 wk). Between the two time periods, the latter appears to be more realistic for CaME, which has a low total PUFAME concentration (26.77 mass%), if it is stored in a dark space absent from moisture. Similar arguments apply to SL_B results for PME (1,430 d [205 wk]; total PUFAME = 9.7 %), SME (378 d [54.0 wk]; total PUFAME = 62.09 %) and MeC18:1 (4,500 d [643 wk]; no PUFAME). Both sets of results could be realistic for MeC18:2 (SL_A : 3.12 d [0.45 wk]; SL_B : 4.83 d [0.69 wk]; 99.0 % PUFAME). Given these considerations, it is concluded that the extrapolation of **Model B** type equations to lower temperatures yielded more realistic shelf-life results (SL_B) than similar processing of **Model A** type equations (SL_A).

Calculation of Activation Energy from Model B

It was proposed in an earlier study (Dunn, 2008) that kinetic parameters for the oxidation of biodiesel can be obtained from solutions to **Model B** type equations. The rate of increase in the degree of conversion of a substrate (α) is expressed by:

$$d\alpha/dt = k_T f(\alpha) \quad (17)$$

where k_T is the reaction rate constant, described mathematically in Eq. 5, and $f(\alpha)$ mathematically describes the kinetics of the reaction. Rearranging and integration yields the following relationship:

$$g(\alpha) = k_T [\tau] t \quad (18)$$

where $g(\alpha)$ is determined from $f(\alpha)$ using Eq. 9 and $[\tau]t$ is the time interval ($t - t_0$). At the induction period of the reaction, $IP = [\tau]t$ where $g(\alpha)$ is determined between $\alpha = 0$ at t_0 and $\alpha = \alpha^*$ at $t = t^*$ ($[\tau]t = t^* - t_0$). Substituting Eq. 5 for k_T in Eq 18, taking the natural log of both sides and rearranging yields:

$$\ln([\tau]t) = \ln[g(\alpha)/Z_0] + (E_a R_g^{-1})(T)^{-1} \quad (19)$$

When $[\tau]t = IP_R$, Eq 19 is equivalent to Eq. 3, the **Model B** type equations derived in the present study. Therefore, kinetic parameters E_a and Z_0 for the oxidation reaction can be calculated from the slope and intercept coefficients from model equations for each FAME. Earlier, an expression was given for calculating E_a from the slope coefficients (B_1) in Eq. 6. The following equation can be used to obtain pre-exponential factor Z_0 from the intercept coefficients (B_0) assuming the kinetic models are known:

$$Z_0 = g(\alpha)[\exp\{-B_0\}] \quad (20)$$

If the reaction kinetics are not known, then Eq. 20 can be rearranged to yield a ratio of Z_0 over $g(\alpha)$, which allows calculation of Z_0 (and k_T) for varying models:

$$[Z_0/g(\alpha)] = \exp\{-B_0\} \quad (21)$$

The results presented in **Table 8** include E_a data and $Z_0/g(\alpha)$ ratios calculated from applying Eqs. 6 and 21 to the **Model B** equation data in **Table 4**. Also shown are estimates for Z_0 factors determined for two popular kinetic models for the oxidation of fatty derivatives, first order (Kamal-Eldin and Yanishlieva, 2005; Litwinienko, 2005; Litwinienko et al., 2000) and “simple” autocatalysis (Adachi et al., 1995; Ishido et al., 2001; Luna et al., 2007). The $g(\alpha)$ functions were determined at $\alpha^* = 0.5$ at the IP_R of the FAME (Dunn, 2020).

Table 8 Activation energy (E_a) and pre-exponential factor (Z_0) calculated from **Model B** equations

FAME	E_a^a (kJ mol ⁻¹)	$[Z_0/g(\alpha)]^b$	Z_0	Z_0
			First-Order ^c	Autocatalysis ^d
CaME	82 (3)	1.92×10^{10}	1.33×10^{10}	8.26×10^{10}
PME	94.1 (0.7)	8.83×10^{11}	6.12×10^{11}	3.79×10^{12}
SME	90 (2)	5.36×10^{11}	3.72×10^{11}	2.30×10^{12}
MeC18:1	120 (6)	8.96×10^{15}	6.21×10^{15}	3.85×10^{16}
MeC18:2	59 (2)	1.91×10^8	1.32×10^8	8.20×10^8

See **Table 1** for abbreviations.

^a Calculated from Eq. 6. Numbers in parentheses are standard errors.

^b Calculated from Eq. 21.

^c Model: $f(\alpha) = (1 - \alpha)$; $g(\alpha) = -\ln(1 - \alpha) = 0.693$ at $\alpha^* = 0.5$ at induction period (IP).

^d Model: $f(\alpha) = \alpha(1 - \alpha)$; $g(\alpha) = -\ln[(1 - \alpha)/\alpha] + C = 4.30$ at $\alpha^* = 0.5$ at IP. C = integration constant [$g(\alpha)$ estimated by numerical integration].

The E_a data in **Table 8** for PME, SME and MeC18:2 were comparable to E_a data obtained from analysis of P-DSC results in an earlier study (Dunn, 2020). On the other hand, results varied significantly for CaME and MeC18:1, with respect to the earlier study. For these two FAME, the values in **Table 8** were -23 kJ mol⁻¹ (lower) and +26 kJ mol⁻¹ for the present work. One study (Litwinienko and Kasprzycka-Guttman, 2000) reported $E_a = 95$ kJ mol⁻¹ for ethyl oleate and 76.0 kJ mol⁻¹ for ethyl linoleate. A literature review in that study suggested E_a values for oxidation were in the ranges 93-100 kJ mol⁻¹ for MeC18:1 and 69-76 kJ mol⁻¹ for MeC18:2.

Results in **Table 8** for the Z_0 factors calculated for the first order kinetic model showed that results for CaME, PME and SME were in a relatively narrow range, between 1.33×10^{10} and 6.12×10^{11} , compared to results for MeC18:1 and MeC18:2. The same general trend was observed in the Z_0 values calculated from the autocatalytic model (range = 8.26×10^{10} to 3.79×10^{12}). For both models, the Z_0 factors for CaME, PME and SME had values that were between Z_0 factors for MeC18:1 and MeC18:2. Studies with ethyl esters reported $Z_0 = 5.66 \times 10^{12}$ for ethyl oleate and 1.45×10^{11} for ethyl linoleate (Litwinienko and Kasprzycka-Guttman, 2000).

In general, there is a paucity of E_a and Z_0 data in the scientific literature for pure FAME and their mixtures (biodiesel). The comparison data described above were obtained from analysis of P-DSC data using model-free kinetic methods. As of this writing, no reliable data from analysis of isothermal induction period (IP_R , etc.) could be identified. Future studies on this topic would justify taking these concerns under consideration.

CONCLUSIONS

The shelf-life of biodiesel is an important property that determines how long it can be stored at low temperatures at fuel terminals and in vehicle tanks and fuel systems. The present work was organized with the

objective of developing mathematical equations for estimating the shelf-life of biodiesel at $T = 25\text{ }^{\circ}\text{C}$ (298.15 K). To meet this objective, two types of models, **Model A** and **Model B**, were obtained from regression analysis where $\ln(\text{IP}_R)$ was expressed as a linear function of T and T^{-1} (Eqs. 1 and 3). While the experimental IP_R data were acquired with measurement temperatures in the range 50-140 degC (323.15-413.15 K), the shelf-life data (SL_A and SL_B) were calculated by extrapolating the model equations to $T = 298.15$ K (Eqs. 2 and 4).

Both **Model A** and **Model B** type equations demonstrated good correlation between $\ln(\text{IP}_R)$ and T (R^2 [?] 0.985) and T^{-1} (R^2 [?] 0.989) and predicting IP_A and IP_B values within corresponding measurement temperature ranges for the five FAME (CaME, PME, PME, MeC18:1 and MeC18:2) studied in this work. Confirmation analysis of these results showed that calculated IP_B data from the **Model B** equations were more accurate than IP_A (from **Model A** equations), with respect to measured IP_R data. Four of the five FAME exhibited lower MAD and RMSD values for calculated results from the **Model B** type equations (exception: MeC18:1).

The shelf-life results from extrapolation of the model equations showed that results from **Model B** (SL_B) were consistently greater than results from **Model A** (SL_A) equations. The results for CaME, PME, MeC18:1 and MeC18:2 demonstrated that SL_B values exceeded SL_A values by an order in magnitude. While **Model A** is traditionally used to estimate shelf-life data in the fats and oils industry, this work showed that extrapolating **Model B** type equations appeared to yield more realistic shelf-life estimates for CaME, PME, SME and MeC18:1. The estimated shelf-life results for MeC18:2 ($\text{SL}_A = 74.8$ h and $\text{SL}_B = 116$ h) seemed too low for realistic storage at $T = 298.15$ K.

Future studies on this topic might include acquiring more experimental data for E_a and Z_0 factors for FAME mixtures under conditions similar to those used to measure IP_R at variable temperatures. Acquiring such data would be helpful in the development of kinetic modeling approaches to estimate shelf-life data for biodiesel at low temperatures. For example, an earlier study (Dunn, 2020) suggested that the autocatalysis model $f(\alpha) = \alpha^{\frac{1}{2}}(1 - \alpha)$ may work well for FAME mixtures that are high in MeC18:1 concentration (Dunn, 2020).

AUTHOR CONTRIBUTIONS

Robert O. Dunn conceived the study, designed the experiments, developed the methodology, supervised technical assistants, organized the data, analyzed the results and wrote the manuscript.

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CONFLICT OF INTEREST STATEMENT

The author declares no conflicts of interest.

ETHICS STATEMENT

No humans or animals were used in this research.

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