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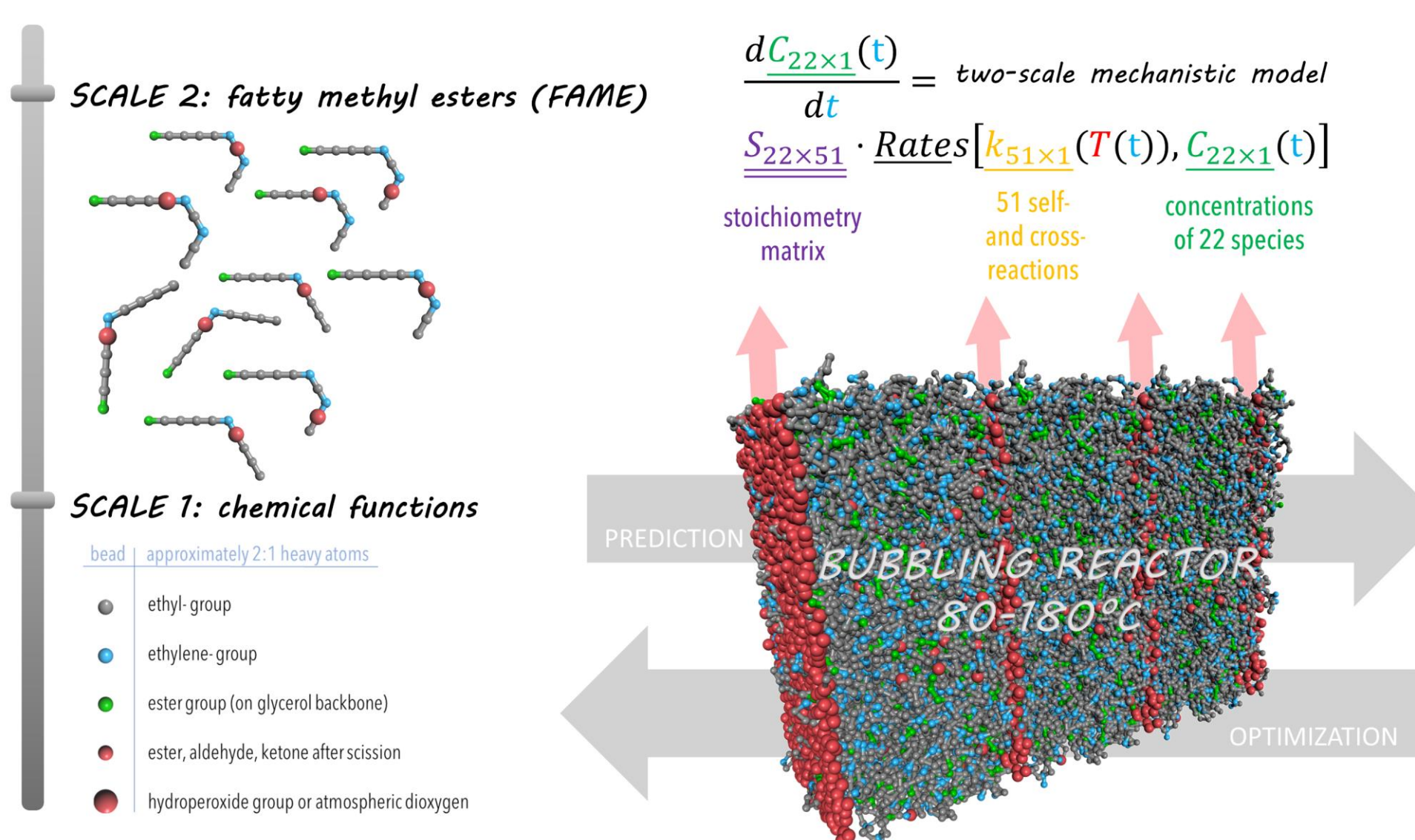
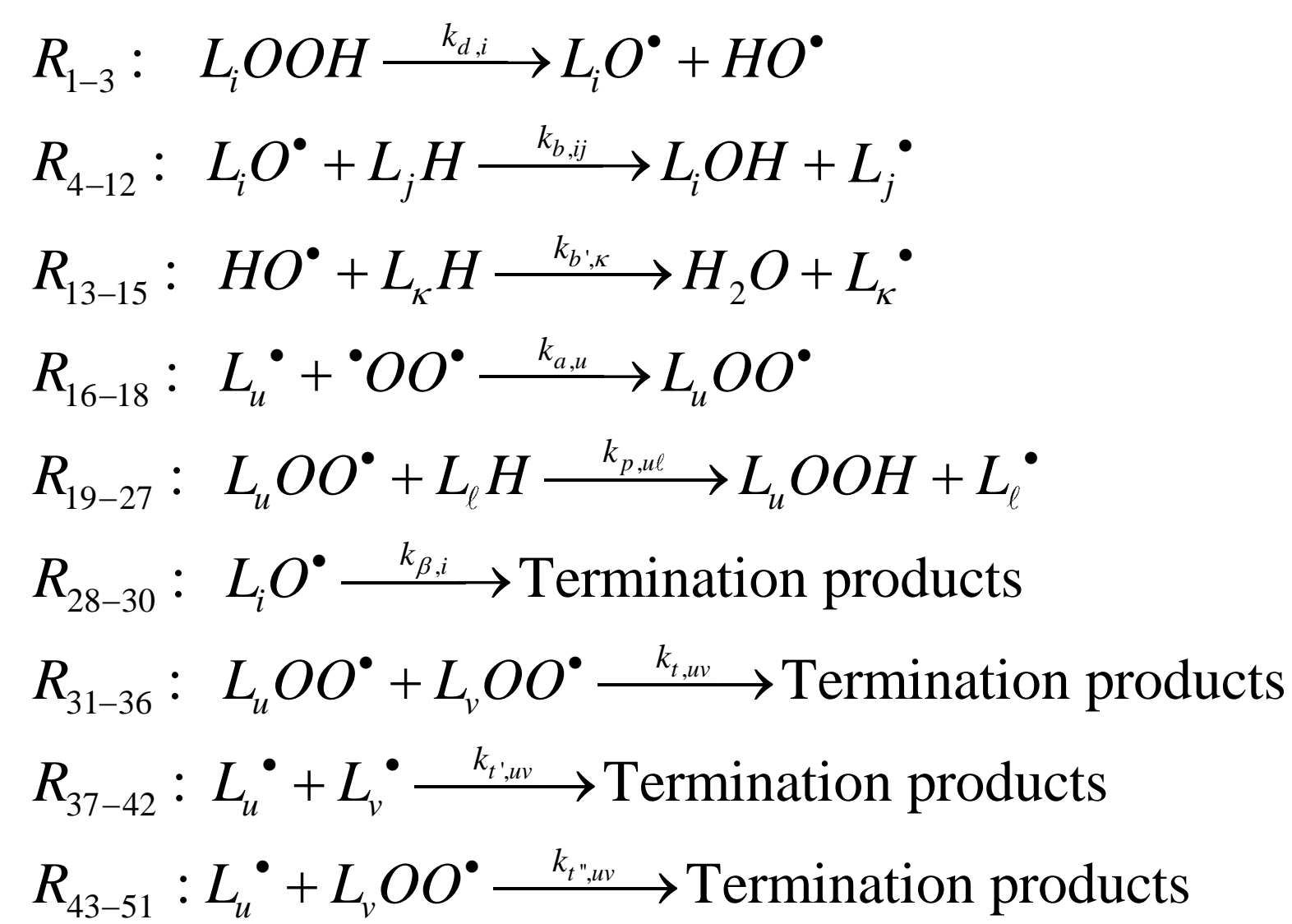
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1. Introduction and objectives

The intricate mechanisms of oil autoxidation and their accurate prediction have long been hampered by the combinatorial nature of propagation and termination reactions involving randomly generated radicals. To unravel this complexity, we suggest a two-scale mechanistic description that connects the chemical functions (scale 1) with the molecular carriers of these functions (scale 2). Our method underscores the importance of accounting for cross-reactions between radicals in order to fully comprehend the reactivities in blends. We rigorously tested and validated the proposed two-scale scheme on binary and ternary mixtures of fatty acid methyl esters (FAMES), yielding three key insights: (1) The abstraction of labile protons hinges on the carrier, defying the conventional focus on hydroperoxyl radical types. (2) Termination reactions between radicals adhere to the geometric mean law, exhibiting symmetric collision ratios. (3) The decomposition of hydroperoxides emerges as a monomolecular process above 80°C [1], challenging the established combinatorial paradigm. Applicable across a wide temperature range (80°C to 200°C), our findings unlock the production of blends with controlled autoxidation stability, optimizing the use of vegetable oils across applications: food science, biofuels, and lubricants.

2. Coupled mechanistic models

2.1. Oxidation pathway and kinetic model



2.2. Coupling with oxygen transfer

$$\frac{d[\bullet OO^\bullet]}{dt} = k_{\bullet OO^\bullet} \frac{A}{V} (S_{\bullet OO^\bullet} p_{\bullet OO^\bullet}^\infty - [\bullet OO^\bullet]) - \sum_{u=1,2,3} k_a [L_u^\bullet] [\bullet OO^\bullet]$$

2.3. Cross-reaction rate constants

Cross-propagation (controlled by the L-H bond dissociation energy) [2-3]

$$k_p = 10^{(13.4 - 0.0478 \times BDE(L-H))}$$

$$k_b = \left(518 \times [H_{allylic}] + 2716 \times [H_{diallylic}] \right)$$

Cross-termination (geometric mean rule) [4]

$$k_{X,ij} = \phi_{ij}^\dagger \sqrt{k_{X,i} k_{X,j}}$$

2.4. Activation and diffusion-controlled reaction [5]

$$k_X(T) = k_X^0 \exp\left(\frac{-E_{a,X}}{R} \left(\frac{1}{T+T_K} - \frac{1}{T_{ref}+T_K}\right)\right)$$

$$k_X^{DC}(T) = \left(\frac{1}{k_X^{SL}(T)} + \frac{1}{k_X(T)} \right)^{-1}$$

2.5. Smoluchowski limit for diffusion-controlled reactions (termination) [6]

From the Stokes-Einstein law [7]

$$D_X(T) = \frac{R(T+T_K)}{6\pi r_X^h \eta(T) N_A}$$

$$\begin{aligned}
 k_X^{SL}(T) &= 4\pi (r_X^g + r_X^s) (D_X(T) + D_X(T)) N_A \\
 &= \frac{16 r_X^g R(T+T_K)}{6 r_X^h \eta(T)}
 \end{aligned}$$

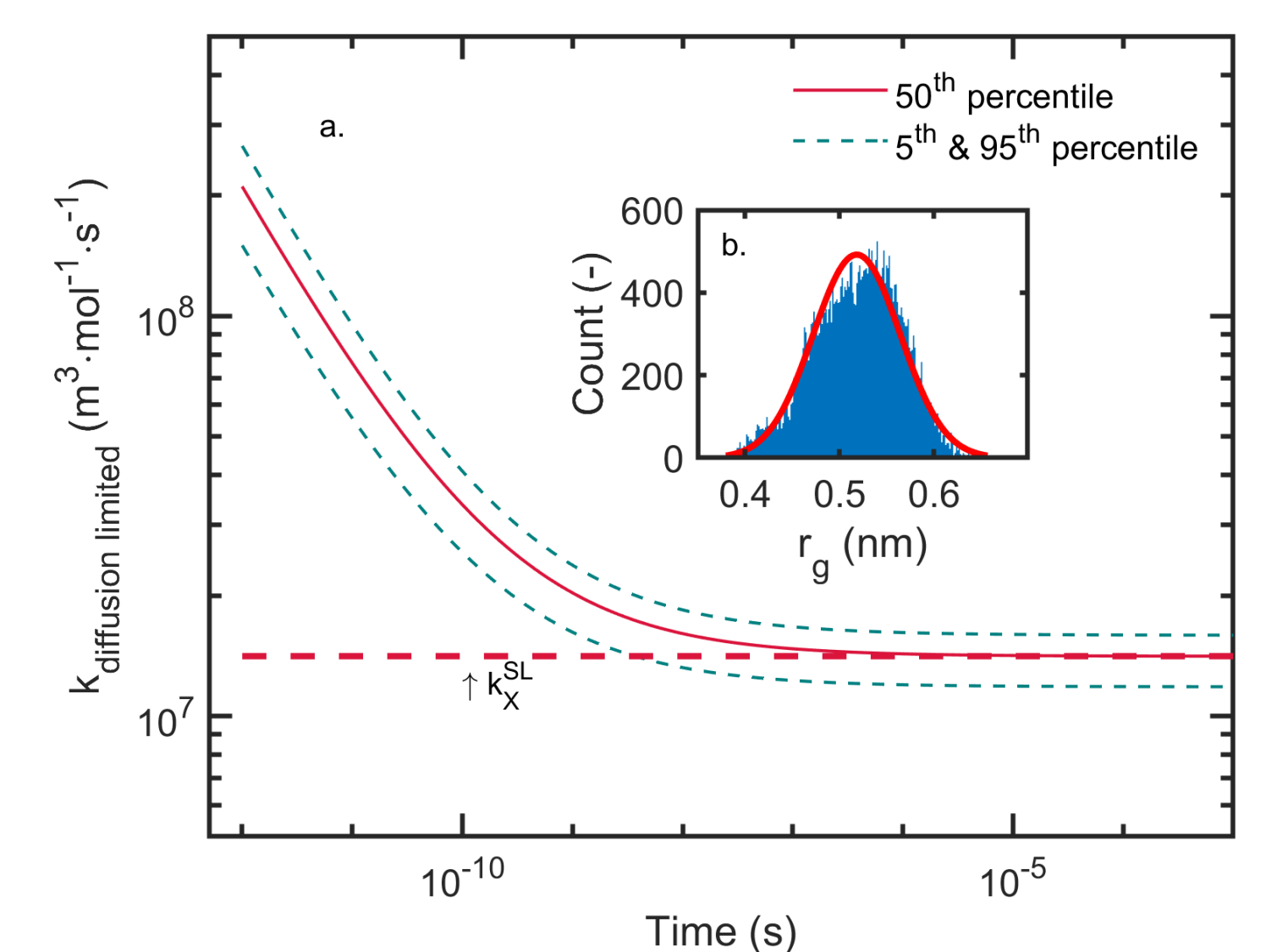


Fig. 1. Example of Smoluchowski limit determination for oleate radicals (a) and radius of gyration (b) at 180°C

3. Results and discussion

3.1. Calibration on pure FAMES

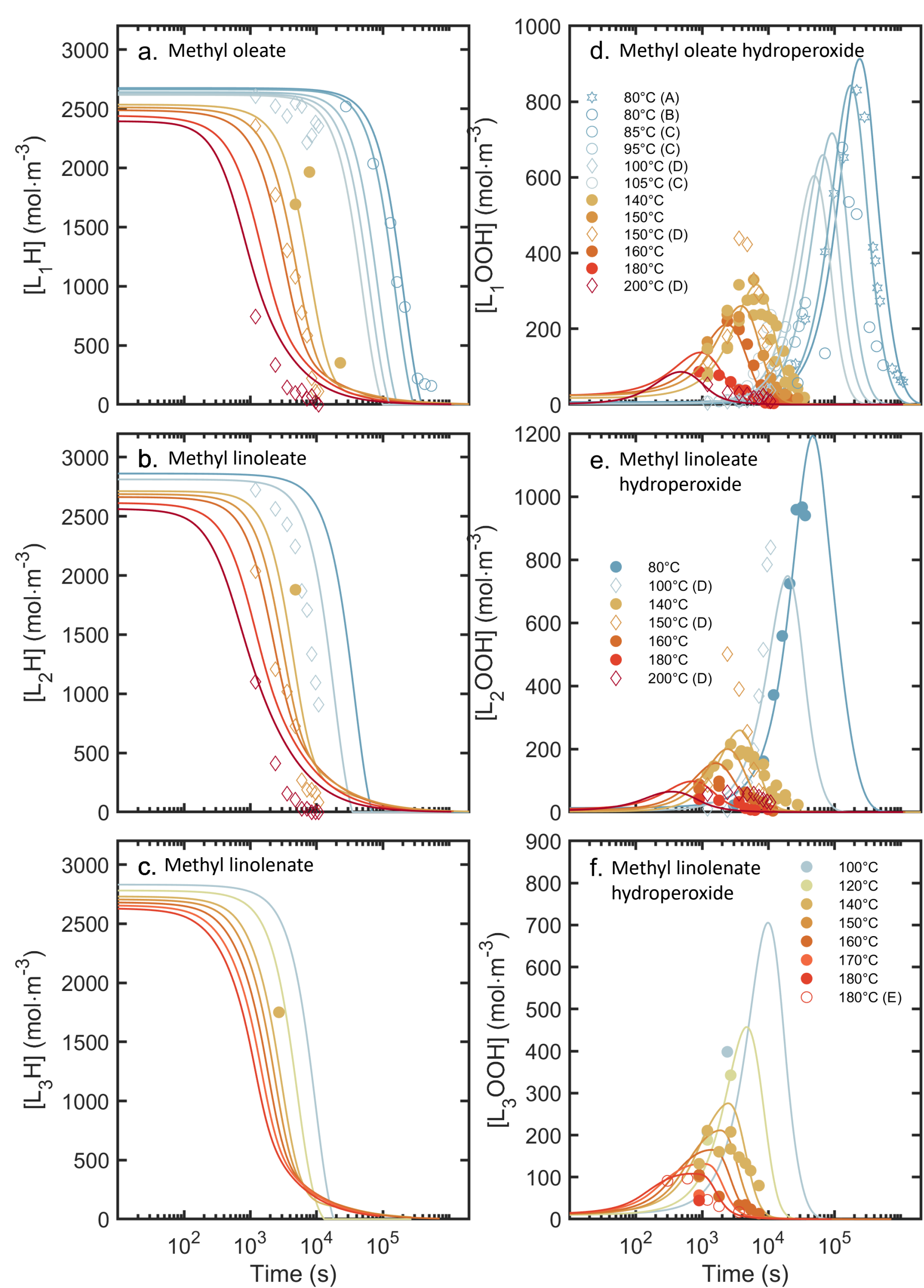


Fig. 2. Kinetics of methyl esters and hydroperoxides (circles and lines are measured and predicted values respectively)

3.2. Validation on FAME mixtures

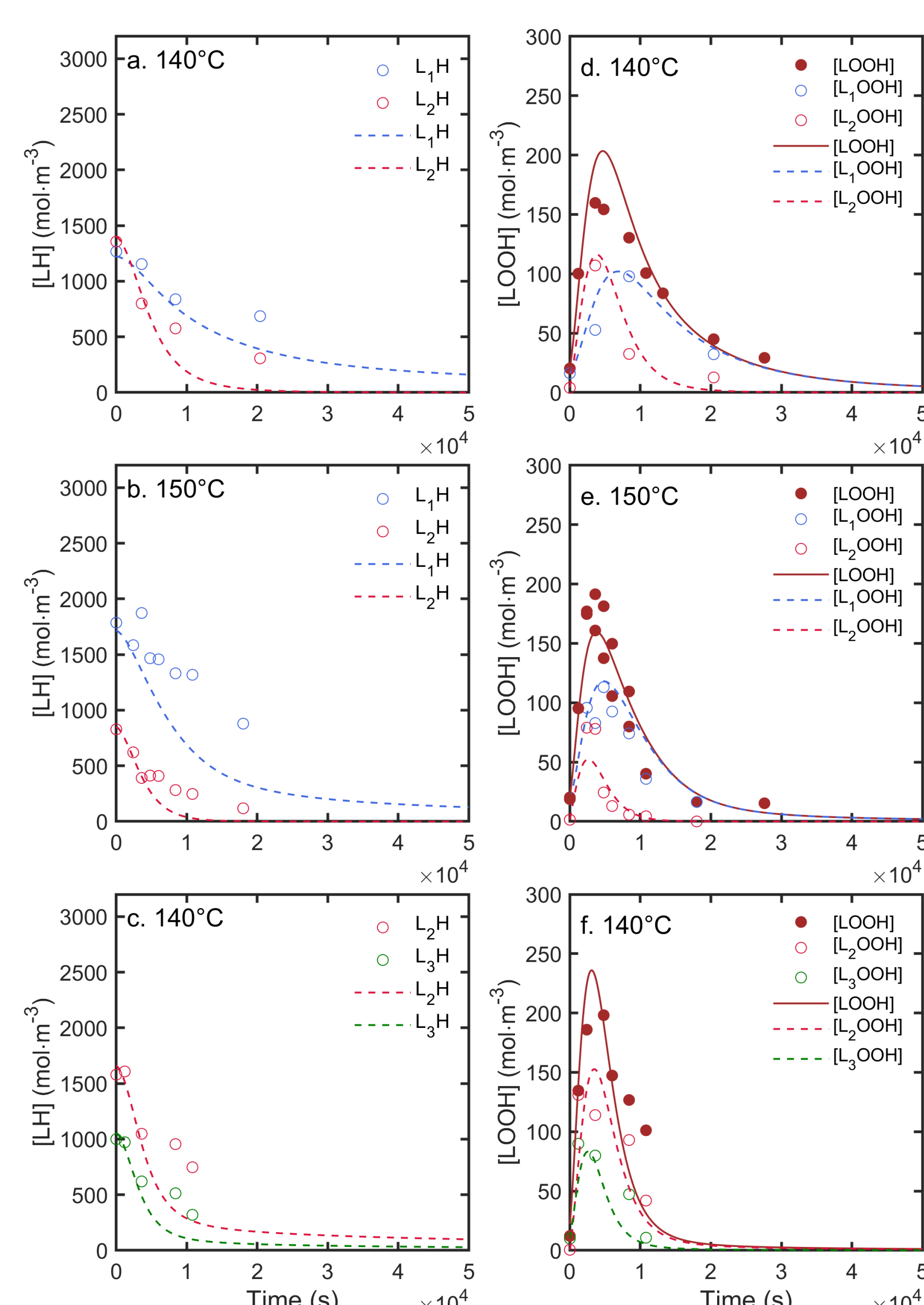


Fig. 3. Kinetics of FAMES oxidation in mixture: 0.5:0.5:0 at 140°C (a,d), 0.7:0.3:0 at 150°C (b,e) and 0:0.6:0.4 at 140°C (c,f) where X:Y:Z are the initial mass fraction of oleate, linoleate and linolenate FAME, respectively

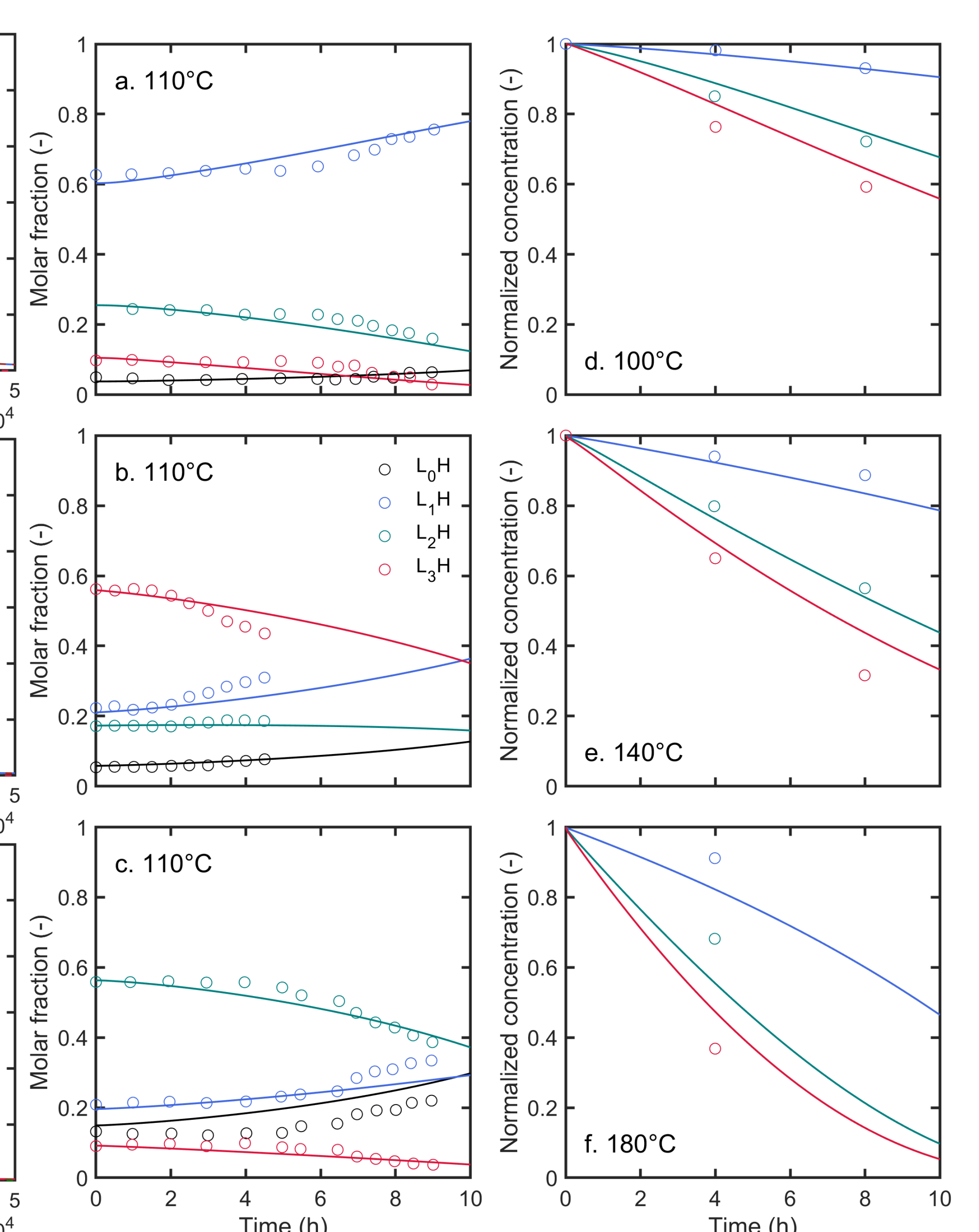


Fig. 4. Evolution of the molar fraction of FAMES from (a) rapeseed, (b) linseed and (c) soybean oil in a Rancimat apparatus at 110°C and rapeseed oil at (d) 100°C, (e) 140°C and (f) 180°C. Experimental data from subplots a-c are from Ref. [8] and d-f from Ref. [9].

4. Conclusion and perspectives

A two-scale combinatorial model for the oxidation of fatty acid methyl ester (FAME) mixtures has been established and calibrated to encompass a variety of cooking, drying, and frying conditions, including temperature, composition of FAMES, and oxygenation. The two scales are tied to the level of detail in the oxidation model: scale 1 focuses on the balance of chemical functions, while scale 2 addresses the carriers of these functions to preserve lineage with the original FAMES.

5. References

- [1] Touffet et al., 2021. Phys. Fluids, 33, 085105; [2] Korcek et al. 1972. Can. J. Chem., 50, 2285; [3] Small et al. 1979. Photochem. Photobiol., 29, 49.; [4] Russell. 1955. JACS, 77, 4583.; [5] Berg & von Hippel. 1985. Annu. Rev. Biophys., 14, 131; [6] Smoluchowski. 1918. Z. Phys. Chem., 92, 129; [7] Miller. 1924. Proc. R. Soc., 106, 724.; [8] Yamane et al. 2007. Int. J. Engine Res., 8, 307.; [9] Baer et al. 2013. el. In 6th International Conference on Biodiesel. Berlin