A comprehensive two-scale model for predicting the oxidizability of fatty acid methyl ester mixtures

Maxime Touffeta, Paul Smitha, Olivier Vitracb[[1]](#footnote-2)\*

aGlobal Core R&D, Cargill R&D Centre Europe, Havenstraat 84, 1800, Vilvoorde, Belgium

bUMR 0782 SayFood Paris-Saclay Food and Bioproducts Engineering Research Unit, INRAE, AgroParisTech, Université Paris-Saclay, 91120 Palaiseau, France

Abstract

The intricate mechanisms of oil thermooxidation and their accurate prediction have long been hampered by the combinatory 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, 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 thermooxidation stability, optimizing the use of vegetable oils across applications: food science, biofuels, and lubricants.

Keywords

Oil thermooxidation, predictive modeling, fatty acid methyl esters, oxidation, co-oxidation, geometric mean rule, hydroperoxides, radical-chain reactions

Highlights

• Introducing a two-scale model for unravelling the oxidation of unsaturated fatty acids in mixtures.

• Validating the model through testing across a range of temperatures (80°C-200°C) and oxygenation conditions using fatty acid mixtures.

• The two-scale approach elucidates species lineage and delivers an entropy and enthalpy interpretation for cross-reactions.

• A compilation of reaction rate constants and activation energies is provided for unsaturated fatty acid, hydroperoxides, and radicals.

# Introduction

Fatty acids are carboxylic acids having an aliphatic chain (saturated or unsaturated) of various lengths ([Moss, Smith, & Tavernier, 1995](#_ENREF_55)). They are found in numerous living systems as they are the main constituent of the bilayer membrane’s cell ([Katsaras & Gutberlet, 2001](#_ENREF_39)) and manufactured formulated products. Fatty acids are available in various chemical forms. Esterified onto a glycerol backbone is the dominant form in food systems such as vegetable oil for deep-frying ([Touffet, Trystram, & Vitrac, 2020](#_ENREF_99); [Vitrac, Trystram, & Raoult-Wack, 2000](#_ENREF_102)), emulsions ([McClements, 2004](#_ENREF_51)), margarine, shortening, chocolate ([Deou et al., 2022](#_ENREF_18)), or cosmetics ([Förster, 2001](#_ENREF_23)), resins ([Dupuis et al., 2017](#_ENREF_19)), paintings ([Pizzimenti et al., 2021](#_ENREF_65)), and lubricant ([Rudnick, 2020](#_ENREF_73)). In biodiesels, fatty acids esterified to methanol are preferred ([Schobert, 2013](#_ENREF_81)).

Regardless of their forms and esterification, fatty acids, especially unsaturated ones ([Brodnitz, 1968](#_ENREF_9)), are susceptible to oxidation. This impairs their functionality ([Runas & Malmstadt, 2015](#_ENREF_74)), nutritional ([Schneider, Porter, & Brash, 2008](#_ENREF_80)), sensorial ([Frankel, 1983](#_ENREF_24)), and mechanical ([Ploeger, Scalarone, & Chiantore, 2009](#_ENREF_66)) properties. The most common mono-, di- and tri-unsaturated fatty esters are oleate (C18:1), linoleate (C18:2), and linolenate (C18:3), which are present in various amounts in soybean, palm, rapeseed, and sunflower oils ([Shahidi, 2005](#_ENREF_84)). These four vegetable oils represent around 87% of the total vegetable oil consumed worldwide in 2022 (approximately 204×106 metric tons) for both food consumption (household and food industry) and industrial uses (biodiesel, green chemistry) ([Statista, 2023](#_ENREF_92)). It is of great interest to reduce the spoilage of these fatty acids by oxidation. The oxidation process transforms molecular oxygen (dioxygen) into organic oxygen incorporated in cascade throughout various oxygenated organic compounds ([Touffet, Patsioura, Ziaiifar, Eveleigh, & Vitrac, 2018](#_ENREF_98)). The first steps involve the dissolution of oxygen in liquid oils and fats and the abstraction of labile hydrogens of the unsaturated fatty esters in α-positions of unsaturations by oxygen-centered radicals peroxyl, alkoxyl, and hydroxyl ([Frankel, 2012](#_ENREF_26); [Frankel, Garwood, Khambay, Moss, & Weedon, 1984](#_ENREF_27); [Frankel, Garwood, Vinson, & Weedon, 1982](#_ENREF_28)). Triplet oxygen is a di-radical and the most common allotrope of dioxygen capable of attacking the alkyl radical produced previously. The reaction led to products with a free valence (unpaired electron), which will propagate until two radicals recombine together to decrease the number of free valences.

Modeling of lipid oxidation has shown a renewed interest during the last decade ([Navaneeth, Kumar, Mehta, & Hermanns, 2017](#_ENREF_56); [Patsioura, Ziaiifar, Smith, Menzel, & Vitrac, 2017](#_ENREF_63); [Richaud et al., 2012](#_ENREF_70); [Richaud, Fayolle, Verdu, & Rychlý, 2013](#_ENREF_71); [Schroën & Berton-Carabin, 2022](#_ENREF_82); [Touffet, Allouche, Ariane, & Vitrac, 2021](#_ENREF_97)). It is often described through lumped mechanisms although different fatty esters exhibit different reactivities to oxidation ([Brodnitz, 1968](#_ENREF_9); [Fatemi & Hammond, 1980](#_ENREF_22); [Korcek, Chenier, Howard, & Ingold, 1972](#_ENREF_42); [Richaud et al., 2012](#_ENREF_70); [Schaich, 2005](#_ENREF_78); [Touffet et al., 2021](#_ENREF_97)). Eventually, oxidation occurs mainly through combinatory mechanisms between species having different reactivities ([Fatemi & Hammond, 1980](#_ENREF_22)): vegetable oils are mixtures of esterified fatty acids, co-oxidation can happen between biodiesel and thermoplastic polymers in contact ([Richaud et al., 2013](#_ENREF_71)), antioxidants compete with fatty acids ([Frankel, 1996](#_ENREF_25)), co-oxidation of protein and lipid can happen in many food systems ([Berton-Carabin, Schröder, Rovalino-Cordova, Schroën, & Sagis, 2016](#_ENREF_8); [Schaich, 2008](#_ENREF_79)). The representation of the chain reaction is also complicated by the presence of several chemical functional groups attached to the same backbone (e.g., glycerol, thermoplastic polymers, and resins). The mass balance in species may not match the one for chemical functions. Chemical functional groups may diffuse independently of chemical species, such as the Waite’s cage diffusion theory ([Waite, 1957](#_ENREF_103)). As in diffusion-controlled reactions, reaction rates may be strongly affected by the density and viscosity of the considered medium ([Waite, 1958](#_ENREF_104)). These complications hinder the determination of bimolecular cross-reaction rate constants between species originating from different substrates ([Fatemi & Hammond, 1980](#_ENREF_22); [Richaud et al., 2013](#_ENREF_71)). From a chemical point of view, the occurrence of co-oxidation of one fatty acid methyl ester (FAME) by-product originating from a different FAMEs has been pointed out since the 1940s ([Farmer & Sundralingam, 1942](#_ENREF_21); [Fatemi & Hammond, 1980](#_ENREF_22); [Gunstone & Hilditch, 1946](#_ENREF_32); [Wong & Hammond, 1977](#_ENREF_108)). However, few papers have since quantified the kinetics of interacting FAMEs during oxidation. As reviewed by [Denisov and Afanas'ev (2005)](#_ENREF_17), Russell and Williamson were the first to study the co-oxidation of various hydrocarbons (cumene, tetralin) and ethers ([Russell, 1955](#_ENREF_75); [Russell & Williamson, 1964a](#_ENREF_76), [1964b](#_ENREF_77)). Their pioneer works was inspirational for the subsequent development of oxidation kinetic models in thermoplastic homo-polymers and co-polymers ([Colin, Richaud, Verdu, & Monchy-Leroy, 2010](#_ENREF_13); [Decker, Mayo, & Richardson, 1973](#_ENREF_16); [Richaud et al., 2013](#_ENREF_71)). At the border between polymer and FAMEs oxidation, Richaud and co-workers demonstrated that the free valence propagated from unsaturated oleate or linoleate methyl esters to polyethylene in both solid and molten states ([Richaud et al., 2013](#_ENREF_71)). The co-oxidation of FAMEs was only studied by [Navaneeth et al. (2017)](#_ENREF_56) but the model suffered several limitations preventing its generalization to arbitrary FAME mixtures. They considered equivalent decomposition rates for all hydroperoxides (lumped value), which were associated with an effective activation energy of 175 kJ·mol-1, much higher than values reported elsewhere in the literature for oleate, linoleate and linolenate FAME ([Hatate, Kawano, & Sone, 1989](#_ENREF_35); [Kawano, Nakatake, & Hatate, 1989](#_ENREF_40); [Nishiike, Takamura, & Matoba, 2000](#_ENREF_58); [Pokorny, Rzepa, & Janicek, 1976](#_ENREF_67); [Richaud et al., 2012](#_ENREF_70); [Shin & Kim, 1985](#_ENREF_85); [Touffet et al., 2021](#_ENREF_97)). Also, equivalent hydrogen abstraction rates were assumed for peroxyl, alkoxyl, and hydroxyl radicals. Finally, cross-termination reactions between peroxyl radicals were not considered ([Navaneeth et al., 2017](#_ENREF_56)).

The current study and oxidation model overcome previous limitations for predicting the oxidizability of arbitrary FAME mixtures at temperatures between 80°C and 200°C commonly encountered in thermal food processes such as cooking, frying, and drying. The cross-reactions between different forms of oxidized FAME are explicitly accounted in a comprehensive reaction scheme that includes both substrates and their primary oxidation products. The reaction rate constants for radical mixtures are derived from “cross combination ratios” and a generalization of collision theory, as first observed by [Kerr and Trotman-Dickenson (1960)](#_ENREF_41) and further supported by additional experimental evidence ([Garland & Bayes, 1990](#_ENREF_29); [Seres, Görgényi, Körtvélyesi, & Nacsa, 1992](#_ENREF_83)) .

The paper is structured as follows. Section two outlines the two-scale oxidation scheme, along with its assumptions and justifications. The model incorporates two scales to account for the mass balance of chemical functions (scale 1) and FAME carriers (scale 2). The large number of combinations introduced by the radical-chain reaction mechanism lead to 51 chemical reactions encompassing both self- and cross-propagation and termination reactions. Since only self-reactions can be directly studied, the cross-reaction rates were determined using a probabilistic molecular theory at scale 2. Section three describes the oxidation conditions considered in the study, the reference self-oxidation rates for FAMEs, and the methodology used to estimate these rates in mixtures. Section four presents the results on FAMEs. Finally, the main conclusions are summarized in the last section. The study demonstrates that incorporating a second scale in the chain-reaction scheme is an effective refinement for optimizing oil blends and substituting one vegetable oil with another, particularly in the context of a highly competitive market for agricultural raw materials. The inclusion of cross-reactions in simulations should be considered as part of the couplings required by the Computer-Aided Food Engineering (CAFE) framework, as recently reviewed by [Datta et al. (2022)](#_ENREF_15).

# Theory

## Pathways and oxidizability of FAMEs alone or in mixtures

At the first scale, the generally accepted reaction pathways ([Schaich, 2005](#_ENREF_78); [Tobolsky, Metz, & Mesrobian, 1950](#_ENREF_96)) start with the endothermic decomposition of hydroperoxides (LOOH) by the homolytic scission of the LO-OH bond (bond energy between 100 and 160 kJ·mol-1). This process is controversial in the scientific community: it can be unimolecular ([Hatate et al., 1989](#_ENREF_35); [Pokorny et al., 1976](#_ENREF_67); [Privett, 1959](#_ENREF_69); [Touffet et al., 2021](#_ENREF_97)) or bimolecular ([Bateman & Hughes, 1952](#_ENREF_6); [Stannett & Mesrobian, 1950](#_ENREF_90); [Stannett, Woodward, & Mesrobian, 1957](#_ENREF_91)) according to the temperature of oxidation and the concentration of hydroperoxides. A bimolecular mechanism will occur if hydrogen bonds stabilize a cage mechanism ([Śliwiok, Kowalska, Kowalski, & Biernat, 1974](#_ENREF_86)). As described previously, a unimolecular mechanism seems acceptable above 80°C for FAME and is assumed in this work ([Touffet et al., 2021](#_ENREF_97)). Unimolecular decomposition produces two oxygen centered and highly reactive radicals: alkoxyl,, and hydroxyl . Both can abstract rapidly labile hydrogen from unoxidized FAMEs,, and yield alkyl radicals and alcohol, , or . Alkoxyl radical can also undergo β-scission generating relatively stable products but also much more volatile products such as carbonyl compounds and alkanes ([Frankel, 1983](#_ENREF_24)). The complex mass transfer associated with the volatile compounds' desorption is not modeled here. Triplet dioxygen is a stable di-radical (noted  ) reacting rapidly with alkyl radicals  and produces an oxygen-centered radical , named peroxyl radical, which can abstract one labile hydrogen from an unoxidized FAME. It is assumed that only the most labile hydrogen is removed according to the unicity of the reactive site rule ([Verdu, 2012](#_ENREF_101)). When the concentration of peroxyl radicals is sufficiently high, they can react together to produce stable termination products such as polymers and volatile compounds ([Frankel, 1983](#_ENREF_24)).

Developing a comprehensive scheme is hampered by the combinatorial nature of oxidative radical reactions. Each new radical can react with other species present in the mixture, leading to a myriad of possible new products. The original complexity can be captured by combining a balance of chemical functions (first scale) and unsaturated carriers (second scale) of these chemical functions. The multiple isomers associated with the different possibilities of hydrogen abstraction on allylic sites (see measurements and discussion of [Touffet et al. (2021)](#_ENREF_97)) are lumped into one single effect related to the FAME carrier (scale 2). This description is sufficiently detailed to preserve the origin of all hydrocarbon species in the mixture. By considering three carriers ( with , e.g., for oleic, linoleic, and linolenic esters) and their “lumped” hydroperoxides ( with ) in the original mixture, the evolution of the mixture at (the) two scales is governed by 51 reactions and involves 22 chemical species (11 radicals including triplet dioxygen, 11 non-radical species including 3 hydroperoxides). At sufficiently high temperatures, typically above 80°C, the initiation proceeds via three possible unimolecular decompositions of the “lumped” hydroperoxides (R1-3). The free valence propagates through 24 bimolecular reactions (R4-27). In this description, the free-valence stops to propagate via 23 possibilities of recombining two radicals, identified by termination reactions R28-51. The complete chain-reaction scheme combining scales 1 and 2 is presented in its developed shape in Section 1 of the Supplementary Material; it can be summarized as:



where ,  ,  and  are different FAMEs (scale 2) with , , ,  and and . The chemical functions hold the information at scale 1.

## Combinatorial oxidation kinetics in mixtures at two scales

### Overview of complications brought by cross-reactions at scale 2

Most oxidation studies on edible oils focus on scale 1 and are limited to a simple balance in chemical functions (conjugated dienes/trienes, hydroperoxides, aldehydes, acids). Scale 2 provides additional details on the composition of initial fatty esters and their oxidation products. The principles of transport and recombination of reactive species were discussed by [Touffet et al. (2021)](#_ENREF_97) for anisothermal oil flow in a deep-fryer. Any unsaturated FAME-carrier (oxidized or not) can react with another unsaturated FAME-carrier according to the reactivity rate of the particular bimolecular reaction. For instance, oleate peroxyl radical can abstract a labile hydrogen from unoxidized linoleate or linolenate and vice versa.

Eq. introduces a consistent mass balance of FAME carriers with the following assumptions. The labile hydrogens originate from non-oxidized FAME carriers, and the possibility of producing di-hydroperoxides is discarded (unicity of reactive site hypothesis). Saturated FAMEs act as diluents of unsaturated FAMEs in the mixture and do not propagate oxidation. The subsequent evolution of termination products is not considered. The concentration of reactive species due to the precipitation of stable cross-linked products and the volatilization of breakdown products are neglected.

Despite the higher sophistication brought by scale 2, this study describes the reactivity of mixtures involving three oxidizable FAMEs, which are envisioned as the simplest generic model for edible oils.

The reactions can be classified according to the number of free valences. Odd amounts (one for R4-15 and R19-27 or three for R16-18) propagate the free valence. The addition of triplet dioxygen on one of the three possible alkyl radicals also falls into this category since it is di-radical. The only exception comes from β-scission whose low molecular weight and volatile alkyl radicals produced are ignored. Oxidation reactions terminate when two intermediate radicals (even free valence numbers, oxygen or carbon centered) react together. Because their recombinations are six magnitude orders higher than their propagation, they are all combinatory. They are doubly combinatorial for the type of radical (oxygen or carbon centered) and the carrier. Peroxyl radicals dominate when the partial pressure of oxygen is over 13 kPa whereas alkyl radicals terminate the oxidation scheme in anoxia (below 0.2 kPa). Between these pressures, cross-terminations between alkyl and peroxyl radicals dominate ([Labuza & Dugan, 1971](#_ENREF_43)).

Considering scale 2 requires the separation of self- and cross-reaction rates. Self-reaction rates can be approached considering pure fatty esters or simple triacylglycerols (e.g., triolein). However, cross-reaction rates are harder to calculate and are specific for different interactions. Rates of radical terminations are the most challenging to determine experimentally. Trapping them with a spin-trapping reagent and detecting them by electron spin resonance analysis has been proposed to identify radical reactivity but without information on the free valence carrier ([Chamulitrat & Mason, 1989](#_ENREF_10); [Roman, Maillard, Plessis, & Riquet, 2010](#_ENREF_72)). The reagent must be selected carefully as it could interfere with regular oxidation mechanisms or produce new radicals ([Merkx et al., 2021](#_ENREF_53)). Alternatively, co-oxidation of fluorescent probes ([Ou et al., 2002](#_ENREF_62); [Uotila, Kirkkola, Rorarius, Tuimala, & Metsä-Ketelä, 1994](#_ENREF_100)) offers an estimation of the total radical concentration without the specificity of spin traps.

### Cross-reaction rate constants derived from self-reaction ones

The combinatorial mechanisms of cross-propagation and cross-termination reactions have been investigated since the 1940s in various fields such as electron transfer, polymerization, and oxidation. The relationships between cross-reaction and self-reaction rate constants are given in Table 1.

#### Cross-propagation rate constants

[Niki, Kamiya, and Ohta (1969)](#_ENREF_57) showed that the structure of the peroxyl/alkoxyl radical could influence the rate of hydrogen abstraction due to steric effects. However, these effects are negligible compared to the bond dissociation energy of hydrogen ([Fatemi & Hammond, 1980](#_ENREF_22); [Wong & Hammond, 1977](#_ENREF_108)). By considering that the nature of the hydrogen of the carrier  (scale 2) is the dominant factor, the propagation reaction rate constants for  and  become respectively:



and



#### Cross-termination rate constants

The recombination of peroxyl and alkyl radicals is so favorable that it occurs at very low concentrations (below detection limits). In The Supplementary Material S3-4 it is shown that cross-termination reaction rates are proportional to the geometric mean of self-reaction rates. This kinetic feature is a mathematical property: each reaction rate shares a concentration with the same stoichiometric coefficient. The geometric mean rule is commonly used for co-polymerization and electron transfer reactions (see Table 1). It implies that the cross-reaction rate between  and  , between and , or between  and  reads:



where  and  are the reaction rate constants of termination between two similar radicals , ,  and , respectively.  is the cross-termination parameter, which scales cross-reaction rates respectively to their geometric mean. Its meaning may not be intuitive as the mass balance. It forces a value of 2 when  (radicals with similar shapes and cross-sections) and a value greater than 2 for  (dissimilar radicals). This is demonstrated in the Supplementary Material S3. In the case of strict equivalence between radicals, the corresponding cross-termination rate must deplete twice as fast for radicals to compensate for one radical being consumed instead of two as in self-reactions.

The validity of Eq. has been tested with a laser-induced stimulation generating two pairs of radicals in gas by [Garland and Bayes (1990)](#_ENREF_29). The study identified some deviations with the hard-sphere theory and recommended careful use for species with dissimilar sizes or involving an additional energy barrier. It is shown in The Supplementary Material that the self-oxidation and cross-oxidation of very similar molecules, such as cumene and α-methyl styrene, lead to  values close to 2. For comparison, the cross-oxidation of cumene and tetralin at 90°C involves the self-termination reaction of tetralylperoxyl, which is 500 times higher than cumylperoxyl termination. The corresponding cross-termination parameter  lies between 5 and 12 according to the composition of the mixture ([Russell, 1955](#_ENREF_75)). Since the self-termination reaction rates originating from oleate, linoleate, and linolenate are of the same order of magnitude (see Table 2),  was expected to be close to 2.

### Assembled kinetic model

The kinetic oxidation model is based on the assumption that it adheres to the mass action law. In this context, the rate of each reaction is directly proportional to the product of the concentrations of the reactants (moieties). At any time, the macroscopic concentrations of the different moieties are assumed to be uniform and not subject to significant macroscopic gradients. For dioxygen, this necessitates the use of a bubbling system or similar method to ensure a spatially uniform production of hydroperoxides.

Reaction scheme involves several bimolecular reactions, which in turn introduce some coupling with molecular-scale transport. Radicals involved in propagation reactions can react with stable products without requiring the mean free paths of their carriers to be significantly larger than their end-to-end distances. These conditions are highly likely in the case of edible oils and undiluted FAMEs, as labile hydrogens are relatively ubiquitous. Under these conditions, bimolecular reactivities involving one stable moiety are assumed to be governed by chemical barriers rather than molecular transport. In contrast, termination reactions involving the encounter of two highly unstable radicals are expected to be significantly more influenced by molecular transport. Possible steric effects are captured at scale 2 by assigning reaction rates specifically to each pair of moiety. All stable reaction products are assumed to be rapidly dispersed and not to hinder subsequent reactions.

Eq. was concisely modeled as a reaction network involving only elementary reactions, each of them occurring in one single transition step. This efficient representation captures efficiently all loops induced by the regeneration of the most reactive species, even when the overall reaction rate equals the rate of all combined initiation steps (*i.e.*, when chain reaction length approaches unity). Using matrix notations, it reads:



where  stands for the matrix product operator,  is the 22×51 stoichiometry matrix (Section 2 of the Supplementary Material).codes reaction rates into a 51×1 column vector of reactions, whose general term for reactants  and  is given by . is a 22×1 column vector coding for the concentration of each species. A detailed description of  and  is given in Section 2 of the Supplementary Material.

### Temperature activation models when at least one of moiety is a stable compound (decomposition, addition)

Absolute reaction rates can be determined using Eyring theory; however, this necessitates prior knowledge of the reactants' energy distribution. [Magee (1952)](#_ENREF_46) initially observed that significant deviations from thermal distributions are expected in "hot" reactions involving radicals and molecules far from their ground states. For the sake of applicability and without sacrificing generality, the rates of self-reaction were assumed to be temperature-activated according to an Arrhenius relationship near a reference temperature for both mono and bimolecular reactions:



where  is the reaction rate at  ,  the activation energy (),  the ideal gas constant () and .

Pre-exponential factors and activation energies have been reported mainly for self-reactions and some cross-reactions. Values from the literature are summarized in Table 2.

### Temperature activation models for bimolecular termination reactions

According to [Berg and von Hippel (1985)](#_ENREF_7), reaction rate constants for diffusion-controlled reactions, such as bimolecular terminations between two radicals of equivalent dimension (R31-51), are determined by both a chemical rate and diffusion rate. Using the additivity of waiting times (*i.e.*, reciprocal reaction rates) due to the diffusion process and of the chemical reaction process, the effective diffusion-controlled reaction rate  is defined as the harmonic average of  given by Eq. , and of the Smoluchowski limit (denoted SL) of the reaction rate without energy barrier, :



Eq. enforces that the overall reaction rate cannot be faster than the slowest of the two. The Smoluchowski limit ([Smoluchowski, 1918](#_ENREF_89)) involves the gyration radius and their self-diffusion, , which can be derived from its dependence with its dynamic viscosity  via the Stokes-Einstein law ([Miller, 1924](#_ENREF_54)). The corresponding expression of  reads for two similar radicals:



where  is the Avogadro’s number. Eq. assumes that radical species have similar transport properties than their stable equivalents. The ratio between the gyration radius  and the hydrodynamic radius  is expected to be close to 0.77 ([Tande, Wagner, Mackay, Hawker, & Jeong, 2001](#_ENREF_93)). In this work, the former was determined by Molecular Dynamics simulation and equals approximatively 0.52 nm ± 0.08 nm. The details are reported in Section 5 of the Supplementary Material. It is emphasized that the SL condition requires that the distance between two radicals is greater than 3.8 nm, which corresponds to 7-to-8 times the gyration radius of the FAMEs carriers. Based on the simulated concentrations of radical species, this condition was always fulfilled. Radical concentrations are always close to zero (e.g., 10-5-10-4 mol⋅m-3 at 180°C) due to their very high reactivity.

The dynamic viscosity model with temperature was fitted from the values reported by [Albert (1938)](#_ENREF_1), [Pratas et al. (2010)](#_ENREF_68) and [Gouw, Vlugter, and Roelands (1966)](#_ENREF_30) as:



Eq. was assumed to be applicable to all studied FAMEs with  = 1.9·10-3, 1.6·10-3 and 1.5·10-3 for oleate, linoleate and linolenate methyl ester, respectively.

### Summary of reaction rate constants

Table 2 summarizes the reaction rate constant models available from literature and their activation by temperature according to Eqs. -. The termination reaction rates requiring the use of Eq. appear with the exponent DC (diffusion-controlled).

## Coupling with oxygen mass transfer at the air-oil interface

Eq. takes into accounts the finite dissolution rate of dioxygen, assuming local thermodynamical equilibrium at the interface between air bubbles and oil. The addition of oxygen onto alkyl radical converts dissolved mineral oxygen into organic one (hydroperoxides) capable of propagating the free valence in the liquid phase (see [Touffet et al. (2021)](#_ENREF_97)). The coupling with the kinetics of oxygen dissolution into the medium is discussed by [Patsioura et al. (2017)](#_ENREF_63). By generalizing the coupling at scale 2, that is by accounting for all possibilities of adding oxygen on available alkyl radical carriers, the mass balance of oxygen reads:



where  is the interfacial mass transfer coefficient of oxygen;  is the oil surface area exposed to air, through air bubbles and the top open surface ;  is the oil volume of oil;  the solubility coefficient of oxygen in the medium;  is the partial pressure of oxygen in the bubbling air;  is the reaction rate constant of oxygen addition on alkyl radical. The addition is so fast that it was assumed to be equiprobable for all alkyl radical carriers ([Hasegawa & Patterson, 1978](#_ENREF_34); [Marchaj, Kelley, Bakac, & Espenson, 1991](#_ENREF_48)).

The solubility coefficient of oxygen in FAME mixtures cannot be derived directly from triacylglycerol ones as they have intrinsically higher free volumes. A general model was developed and validated on the extensive solubility data sets and early models reported in the literature on butyl oleate ([Arai, Yoshitama, Nishihara, & Sano, 1989](#_ENREF_2); [Bateman & Gee, 1951](#_ENREF_5); [Jarvi, 1972](#_ENREF_38)). By considering  is the molar volume of the considered FAME ([Pratas et al., 2010](#_ENREF_68)), the solubility in mol⋅m-3⋅Pa-1 reads:



The constants  are from [Arai et al. (1989)](#_ENREF_2) and are assumed independent of the considered FAME. They are equal to 7080, 56.603, -0.11064, and -309.62, respectively. By considering that specific volumes are additive, the oxygen solubility for a mixture are defined as the volume average of oxygen solubilities of each FAME

# Materials and Methods

## Studied FAMEs and FAME mixtures

Methyl oleate (96% purity), linoleate (99% purity) and linolenate (99% purity) were purchased from Alfa Aesar, Acros Organics and Sigma Aldrich, respectively. The composition of studied FAME mixtures are listed in Table 3. Fresh FAMEs and FAME mixtures do not contain antioxidants.

## Bubbling reactor and oxidation conditions

Oxidation reactions were conducted in the miniaturized bubbling reactor described by [Touffet et al. (2021)](#_ENREF_97). Around four grams of pure FAMEs and mixtures were poured in the reactor and oxidized between 80°C and 180°C. Binary mixtures of different FAMEs were prepared by weighting and mixing different amounts of pure FAMEs.

## Determination of total hydroperoxide content by Differential Scanning Calorimetry (DSC)

The total hydroperoxide content,, was determined by DSC according to method already described by [Mallégol, Gonon, Commereuc, and Verney (2001)](#_ENREF_47). A small aliquot (10-20 mg) of FAME or FAME mixture previously oxidized in the bubbling reactor was heated from 25°C to 250°C at a rate of 3°C·min-1 under nitrogen flow. The decomposition of the hydroperoxides in the pan and the exothermic combination of produced radicals enabled a direct quantification of hydroperoxides, by assuming an apparent enthalpy of 320 kJ·mol-1.

## Quantification of unsaturated FAMEs and their hydroperoxides

Unsaturated FAMEs and associated hydroperoxides (except methyl oleate hydroperoxides) were separated and quantified by high performance liquid chromatography equipped with a diode array detector (RT-HPLC-DAD). The protocol is similar to the one described by [Crouvisier Urion, Garcia, Boussard, Degrand, and Guiga (2022)](#_ENREF_14) and summarized hereafter. A Thermofischer C30 Accucore column (2.6 µm, 150 mm × 2.1 mm) was used with a mobile phase of water (A)-acetonitrile (B), both containing 0.1% formic acid and 5% THF. A gradient elution was adopted with the following program: initially 5% B linearly increased to 63% B in 3.0 min, kept at 63% B from 3.0 to 10.0 min, then linearly increased to 85% from 10.0 to 11.0 min and maintained at 85% B from 11.0 to 15.0 min, and returned to 5% in 1.0 min and maintained 5.0 min. The flow rate was 0.25 mL⋅min-1. Methyl oleate, linoleate, and linoleate were detected at 205 nm for retention times of 19.1 min, 18.2 min, and 17.4 min, respectively. Methyl linoleate and linolenate hydroperoxides were detected at 234 nm for a retention time of 15.9 min and 15 min, respectively. Methyl oleate hydroperoxides were not identified, but their concentrations were estimated by considering with  according to the binary mixture studied.

## Numerical resolution and required software

The ordinary differential equation (ODE) system (Eq. ) was integrated numerically for proper initial condition and possible variable temperature with Matlab (The Mathworks Inc, Natick, Massachussets, USA). The capability of standard ODE solvers to solve the two-scale approach was tested on Matlab versions from R2011a to R2022a. Similar checks were carried out with the last open-source GNU-Octave (LSODE version 7.1) and integrate.ode of the Python library SciPy (version 1.11). Considerations about the stiffness and stability of the numerical scheme to choose are discussed specifically in section 4.4.

# Results and Discussion

## Oxidation kinetics of pure FAME: consistency of self-propagation and radical cross-termination reactions

The kinetics of FAME consumption and hydroperoxide accumulation at various temperatures are presented in Figure 1 under non-limiting oxygen dissolution conditions at atmospheric pressure. This condition corresponded to a volumetric mass transfer coefficient or higher, with the minimum value determined for methyl linolenate (the most reactive FAME in this study). The experimental curves for  (methyl oleate),  (methyl linoleate),  (methyl linolenate), and their hydroperoxides are presented in Figure 1 for temperatures ranging from 80°C and 200°C. Oxidation kinetics obtained in this work are compared with similar kinetics from the literature at lower temperatures. The same continuous evolutions were predicted from first principles by solving Eqs. - for the reaction scheme adapted to pure FAMEs (nine reactions instead of fifty-one). Corresponding pre-exponential factors and activation energies are summarized in Table 4. It is worth noting that the model described all data well without any fitting and could reconstruct the missing parts of the kinetics or extend the oxidation kinetics beyond the observed duration period.

For all tested temperatures, hydroperoxides accumulated until a maximum value (chain reaction length decreased down to unity) and then decreased (chain reaction length increased). The maximum concentration in hydroperoxides indicated when the condition of steady state was reached, meaning the addition of oxygen was as fast as the bulk thermal decomposition of oil ([Patsioura et al., 2017](#_ENREF_63)). The steady state condition was approximately maintained while the number of labile hydrogens locally exceeded the number of oxygen-centered radicals. At high oxidation rates, the termination reactions through peroxyl radicals progressively increased. Lower temperatures delayed the time to reach steady state. An induction period was detectable below 100°C, but not above. At temperatures above 100°C, the decomposition of hydroperoxides occurred much more rapidly, with half-lives around 50 min (for oleate), 15 min (for linoleate) and ~ 5 min (for both) at 140°C and 180°C, respectively, as previously reported by [Touffet et al. (2021)](#_ENREF_97). These features at scale 1 are captured in Table 4 by the highest activation energies of the homolytic decomposition of hydroperoxides (values ranging from 60 and 81 kJ⋅mol-1) compared to termination reactions (values ranging from 35 and 60 kJ⋅mol-1) and propagation ones (values ranging from 27 and 47 kJ⋅mol-1).

At scale 2, the results demonstrate that the consumption of linolenate fatty esters occurred more rapidly than that of linoleate and oleate esters across all studied temperatures. The induction time to reach steady state half as long at 140°C. This can be attributed to the higher lability of hydrogens and the higher number of bis-allylic sites. The maximum concentration of hydroperoxides was similar for linolenate and linoleate, which confirmed the similar stability of their hydroperoxides. A sharp decrease in pure FAME was a common feature, with the inflection point corresponding to the maximum level of hydroperoxides. The increasing instability of hydroperoxides with temperature was the cause of the acceleration of oxidation. Oxidation is self-induced in the case of pure FAMEs.

## Cross-oxidation kinetics of FAME mixtures

Cross-oxidation kinetics of FAME were investigated in binary and ternary mixtures between 110°C and 180°C. The parameters validated on pure FAMEs were generalized to their mixtures by considering that the hydrogen donor controlled propagation (H-carrier, see Eqs. -) and that termination reactions between radicals adhered the geometric-mean rule (see Eq. ).

### Binary mixtures of FAMEs

Binary mixtures underwent oxidation in the same conditions as pure FAMEs at 140°C and 150°C in non-limiting oxygenation conditions. Experimental data and predictions with the reaction scheme (Eq. , including 51 reactions and 22 species) are compared in Figure 2 for  and . Pair cross-termination parameters were set to 2 based on observations at 140°C. A value close to 2 indicated symmetric behavior. An independent validation is given in Figure 3 by comparing predictions with oxidation kinetics reported in the literature ([Cherepanova & Sapunov, 2022](#_ENREF_12)) at 110°C without any adjustment.

The two-scale model successfully reproduced the kinetics observed experimentally in this study for global (scale 1) and specific chemical species (scale 2). In initially homogeneous mixtures of oleate and linoleate ( with equi-concentrations, see Figure 2a,d), oxidation was initiated and propagated through the linoleate chain reaction, leading to rapid accumulation of hydroperoxides in the mixture. The production of oleate hydroperoxides began simultaneously but at a lower intensity. They became dominant later in the mixture when the amount of linoleate FAME has already decreased by half. At scale 1, one maximum concentration in hydroperoxides was observed. At scale 2, the maxima of the two populations of hydroperoxide (L1OOH/L2OOH and L2OOH/L3OOH) are distinguishable. Due to the faster consumption of linoleate FAME and lower stability of linoleate hydroperoxides, their concentration diminished more rapidly. After 2·104 s, almost all hydroperoxides were oleates. The mixture of linoleate/linolenate FAMEs at 140°C (Figure 2f) displayed a more pronounced peak in hydroperoxide kinetic (rapid accumulation and decomposition).

[Cherepanova and Sapunov (2022)](#_ENREF_12) reported the oxidation kinetics at 110°C of two binary FAME mixtures with two different initial methyl oleate-to-methyl linoleate ratios: 0.91:0.09 (trans-esterified with methanol from olive oil) and 0.26:0.74 (from sunflower oil). They measured the depletion kinetics of each species and the total accumulation in hydroperoxides. The capability of extrapolating oxidation kinetics at temperatures and for compositions different from those previously studied is shown in Figure 3. The two-scale predictions were remarkably accurate and confirmed the choices of cross-termination parameters close to 2. Moreover, the two-scale model explained the difference in the duration of the steady state according to the ratio L1H:L2H. At high L1H concentration, the L2Hs initiate oxidation and propagate it to L1Hs. These consume the hydroperoxides more slowly than the L2H due to a less efficient abstraction of labile hydrogens and higher thermal stability. The maximum hydroperoxide concentrations are similar, but overall correspond to a lower number of propagation events.

### Ternary mixtures of FAMEs

Experimental oxidation kinetics of FAMEs, produced by transesterification of edible oils (rapeseed, linseed, and soybean oils) with methanol, were obtained in a Rancimat apparatus by [Yamane et al. (2007)](#_ENREF_110) and [Baer et al. (2013)](#_ENREF_4) at temperatures ranging from 110°C to 180°C . These studies served as references of ternary mixtures of FAMEs for comparison with our two-scale model. Saturated fatty esters present in the mixture were considered stable during the experiment duration. This assumption was justified, especially at temperatures below 140°C, since the abstraction rate constant of aliphatic hydrogen abstraction by peroxyl radicals is about 1.3·10-6 m3·mol-1·s-1 at 110°C ([Korcek et al., 1972](#_ENREF_42)) and remains much lower than those of hydrogens in allylic and bis-allylic positions (see Table 4). In addition, it has been demonstrated that the Rancimat conditions do not offer sufficient oxygenation to fulfill the oxygen dissolution rate-to-oil volume ratio set in Figure 9 of [Patsioura et al. (2017)](#_ENREF_63). The predictions with the full reaction scheme (51 reactions) were carried out for and without additional assumptions. The experimental values and predictions are compared in Figure 4 without any mathematical adjustment. The results are expressed in molar fractions as in the original work to facilitate the comparison and highlight the relative concentration in stable species observed by authors.

The predictions of the two-scale model were consistent with experimental results for the entire range of temperatures studied. In all tested conditions, the relative content of saturated and monounsaturated FAMEs increased with time due to the oxidation of polyunsaturated FAMEs. The two-scale model showed accuracy when the amount of saturated FAMEs in the mixture was low (see Figure 4c). For FAMEs from soybean oil, the molar fraction of saturated FAMEs was slightly overestimated by the two-scale model, and unsaturated ones were correspondingly underestimated. Saturated fat could indeed have been slightly oxidized by highly reactive hydroxyl and alkoxyl radicals. Despite these limitations, the two-scale model accurately captured oxidation activation by temperature (Figure 4d-f).

## On the relative importance of termination reactions of oleate/linoleate mixtures

The two-scale model enables tracking of reactivities in mixtures beyond experimental capacities. Specifically, the relative importance of self- and cross-of termination of binary mixtures of oleate/linoleate can be investigated. It is commonly believed that an excessive linoleate content negatively affects oil shelf-life during storage or lifetime under frying conditions. The predicted contributions of the initial fraction in methyl linoleate on cross-termination reactions from oleate and linoleate are analyzed at different oxidation times in Figure 5.

For short oxidation times (Figure 5a), the self-reaction of oleate peroxyl radicals decreases dramatically and becomes marginal as soon as 20% linoleate FAME is incorporated into the mixture. At 30% linoleate content, the self-reactions of linoleate peroxyl radicals dominate and cross-reactions involving linoleate peroxyl radicals accounts for over 90% of all termination reactions. At 70% linoleate content, self- and cross-reactions involving oleate peroxyl radicals are negligible.

For longer oxidation times (Figure 5b-d), as linoleate FAMEs are consumed, oleate peroxyl radicals become more involved in self- and cross-reactions. Methyl linoleate primarily controls oxidation during the initial moments of oxidation due to higher termination reactions, alongside lower thermal stability of hydroperoxides and lower bond dissociation energy of bis-allylic hydrogens.

## Discussion on the benefit of the second scale and the sensitivity to co-oxidation?

The two scale model captures well the co-oxidation mechanism during propagation and termination. The involvement of two scales does not increase significantly the computational cost of the oxidation model. Modern mathematical libraries in C++, Fortran, Matlab, Octave, Scilab, Python, R, MuPAd, Mathematica, and Maple can solve hundreds of coupled ordinary differential equations (ODE). As a rule of thumb, we use the robust variable-step and variable-order ODE solver ode15s implemented in Matlab and derived from the ODE Suite proposed by Shampine and Reichelt ([Lawrence & Mark, 1997](#_ENREF_44)). The mathematical problem is not particularly stiff except at the beginning of the kinetics. It automatically adapts the timestep to approach exponential convergence that other packages, such as CHEMODE cannot achieve ([Aro, 1996](#_ENREF_3); [Falati & Hojjati, 2011](#_ENREF_20)). Several hours of oxidation are simulated in less than one or two seconds of a modern CPU, offering real-time control capability for developing digital twins, optimizing oil formulation, or even coupling the reaction scheme with an oil flow or mass transfer model. In this context, despite the 51 coupled equations, the two-scale approach does not introduce any overhead. From a cognitive perspective, understanding the role of co-oxidation (cross-terms) is more critical, as it will enable us to understand how different oils should be mixed for frying applications. The equivalent optimization problem aims to maximize the unsaturated content to increase the nutritional benefit of frying oil while maximizing oil shelf-life to reduce waste. The co-oxidation contribution is obtained by comparing the kinetics with and without cross-reaction terms. For each species, , present in the reaction scheme, the co-oxidation contribution can be calculated as:



where  and  are concentrations with and without co-oxidation respectively. Since industry relies on total polar compounds (TPC) to measure oxidation, a lumped species “*s*=TPC” was introduced and defined by the balance of all compounds subjected to oxygen addition. Therefore, all stable products originating from alkoxyl or hydroperoxyl radicals were counted as TPC. The likely volatilization of scission products and the precipitation of cross-linked products (polymers) were not considered.

The two-scale model predictions with and without cross-reactions are compared for three typical oil blends in Figure 6. The weight compositions (oleate:linoleate:linolenate) were 0.8:0.1:0.1 (Figure 6a,d), 0.6:0.2:0.2 (Figure 6b,e), and 0.33:0.33:0.33 (Figure 6c,f). The non-limiting oxygen transfer condition was fixed with  . The residual amount in FAMEs, hydroperoxides, and radicals are plotted in Figure 6.

Removing cross-reactions reduces the global rate of oxidation in all the tested mixtures. This confirms the essential role of co-oxidation under frying conditions. The effects are maximal when the concentrations of FAME are similar (Figure 6c,f), and the overall oxidation rate cannot be considered from the superimposition of the three oxidation mechanisms. The oxidation of the most sensitive species accelerates the oxidation of the least sensitive ones. In the long term, the less sensitive species prolong the oxidation of already depleted species. In particular, alkyl and peroxyl radicals from oleate FAME accumulate as long as those from polyunsaturated FAME compete with the abstraction of labile hydrogens and termination reactions. These results exemplified the self-accelerated character of oil oxidation and its lack of specificity once the amount of hydroperoxides reaches a sufficiently high level. From an experimental vantage point, all hydroperoxide mass-balance either lumped (scale 1) or detailed (scale 2) appear mono-modal (a single maximum) at constant temperature and with non-limiting oxygen mass transfer. The coupling via cross-reactions (scale 2) demonstrates that oxidation kinetics cannot be extrapolated to arbitrary oil composition using lumped reaction rate constants.

The corollary is that the unsaturated content with the highest nutritional value can be maintained in the frying oil only if the oil is renewed sufficiently. In this regard, batch deep-fryers do not offer optimal performance, as the oil remains at high temperatures for several hours during heating, holding time, and cooling. Continuous deep-fryers with high oil renewal rates better preserve the polyunsaturated oil content. As a general guideline, it is recommended that the oil’s age does not exceed the induction time required to reach a steady state for the most sensitive species. This time can be extended by slowing down the dissolution kinetics of oxygen, for example by adding a cover, inerting the headspace with nitrogen or steam, or preventing air circulation around the deep fryer. Ultimately, reducing the frying temperature always improves the oil quality.

The predictions of TPC accumulation kinetic during the oxidation at 175°C of different mixtures in non-limiting oxygen transfer condition are plotted with the corresponding  values in Figure 7. The weight compositions (oleate:linoleate:linolenate) were 0.8:0.1:0.1 (Figure 7a), 0.6:0.2:0.2 (Figure 7b), and 0.33:0.33:0.33 (Figure 7c). As described previously, removing cross-reactions reduces the significantly the global rate of oxidation with deviations up to 60 % for TPC (mixture 0.33:0.33:0.33)

Although our two-scale model does account for the distribution of esters rather than triacylglycerols, it demonstrates that any oil with similar ester composition will exhibit comparable oil oxidation kinetics. While blending typically occurs before filling the deep-fryer, regularly adding oil with a high unsaturated content may be justified to maintain the nutritional value of oil throughout the entire production cycle. The frequency of renewal should be comparable to the induction time.

# Conclusions

A two-scale combinatorial model for the oxidation of 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 FAME.

The interactions between different radical species are determined either by assuming a dominant effect or by applying the geometric mean rule. The dominant effect, applied to propagation reactions, is imposed by the reactivity of the labile hydrogen holder, rather than by the type of hydroperoxyl or alkoxyl radical. The geometric mean rule, first hypothesized by [Marcus (1993)](#_ENREF_50), is applied to the recombination of two radicals, regardless of their nature or carrier. This rule has proven robust and only requires the determination of the cross-reaction coefficient. A theoretical value of 2, corresponding to symmetric collisions, works well for nearly tested cases.

The comprehensive chain-reaction model encompasses 51 elementary reactions and the dissolution kinetics of oxygen. The coupled equations can be quickly solved numerically, yielding accurate estimates of various species’ concentrations under both static and dynamic conditions. Temperature, oxygenation, and oil renewal can be readily integrated into the model. To validate the model, meticulous experiments were conducted with binary mixtures of fatty methyl esters (FAMEs), specifically measuring each FAME’s hydroperoxide. The experiments, carried out isothermally and under non-limiting oxygen dissolution conditions, facilitated the determination of both self- and cross-reaction rates. These values as well as the developed model can be used for a wide range of applications. The model was successfully tested for the prediction of the thermal stability of ternary mixtures of oleate, linoleate, and linolenate esters. The critical assumption of unimolecular hydroperoxide decomposition was well verified for all FAMEs, individually and combined, between 80°C and 200°C. Comparing coupled and uncoupled reaction outcomes revealed that cross-reactions play a significant role in enhancing oxidation reactions and extending reaction rates. These effects, which are tied to specific mass balances and reactivities at scale 2, cannot be replicated with lumped coefficients at scale 1.

Despite its successes and ease of implementation, the model has several limitations to consider. One limitation is the assumption of non-reactivity for saturated FAMEs, which is acceptable at low frying temperatures (140°C) but may become less valid at higher temperatures. At high temperatures, the high thermal activation of hydroperoxide decomposition and aliphatic hydrogen abstraction can result in oxidation through saturated FAMEs, as demonstrated by [Thaler and Kleinau (1968)](#_ENREF_95).

Conversely, at low oxidation temperatures, hydrogen bonding between hydroperoxides can stabilize cage effects and promote bimolecular decomposition of hydroperoxides, as reported by [Yablonskii et al. (1972)](#_ENREF_109). At high concentrations of hydroperoxides, bimolecular decomposition is likely to govern induction time, even if the network of hydrogen bonds involved in the stabilization is not yet well understood, as well as the role of dissolved water. The intricate network of hydrogen bonds in oxidized oils may also involve secondary oxidation products such as carboxylic acids and alcohols, as demonstrated by ATR-FTIR measurements ([Touffet et al., 2018](#_ENREF_98)). An oxidation model covering the range from room to frying temperatures should account for the temperature-concentration diagram to determine the appropriate initiation mechanism based on the medium’s polarity.

Additionally, the assumption of equal reactivity for triacylglycerols and FAMEs should be approached cautiously. Notable differences in oxidation rates between ethyl esters and equivalent triacylglycerols have been reported in limiting oxygen dissolution kinetics (Sullivan Ritter et al., 2015), but it is unclear whether these differences in reactivity are due to the structural effect of glycerol reducing the mobility of esterified fatty acids or a difference in oxygen solubility in triacylglycerols and equivalent methyl esters (Roppongi et al., 2021). The rotational or translational diffusivities of triacylglycerols could play a significant role at the molecular level, particularly when the distance between two reactive species becomes larger due to the presence of non-reactive fatty esters. Fatty esters bound to the same glycerol cannot reorient as freely as corresponding FAMEs. According to the Stokes-Einstein law, a dependence of self-diffusivities with the reciprocal square root of the molecular mass is expected for FAMEs and triacylglycerols. The branching of three fatty esters on the same glycerol would cause the diffusivities of triacylglycerols to be a fraction  the FAMEs’ ones. The model does not consider desorption and precipitation of breakdown products, nor does it accounts FAMEs co-oxidation with proteins or carbohydrates during deep-frying, for example. Subsequent papers will address some of these issues in greater detail.

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# Appendix A. Notations

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1. \* Corresponding author. Tel : +33169935063 ; fax : +33169935044 ; *E-mail Address*: [olivier.vitrac@agroparistech.fr](mailto:olivier.vitrac@agroparistech.fr) (O. Vitrac). [↑](#footnote-ref-2)