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Coupling between oxidation kinetics and anisothermal oil flow during deep-fat frying

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Highlights

- description of oil flow and temperature distribution in kitchen appliances during heating and holding times;
- simplified descriptions of the generation and decomposition of hydroperoxides from triacylglycerols as a mixture of fatty esters in frying conditions;
- coupling between Eulerian and Lagrangian descriptions to analyze the effects of residence times at different temperatures;
- validation experiments with a modified and instrumented deep-fryer and reference decomposition kinetics in anoxia.

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Abstract

Deep-fat frying is a cooking technique that has been used continuously since prehistoric times. A domestic deep-fryer heated from the bottom develops significant convection inside the bath cavity. It is responsible for very high heat transfer coefficients and the deep-frying oil exposure to the atmospheric oxygen. The continuous conversion of gaseous dioxygen into unstable and reactive hydroperoxides and their subsequent advection throughout the bulk volume is at the origin of the main complaints made of frying: odors, fouling, and generation of several toxic compounds. This study analyzes the coupling between natural convection of triacylglycerols and the combinatorial chemistry controlling their autoxidation. At macroscopic scale, anisothermal flow within a typical kitchen appliance, including a cold zone beneath the heating element, was simulated in 3D under the Boussinesq approximation with an Eulerian description during initial heating and temperature holding. At molecular and intermediate scales, the endothermic decomposition of fatty-ester hydroperoxides in mixtures was simulated over several hours using a Lagrangian description. Simulations and the proposed description of the combinatorial generation of hydroperoxides highlighted the complex relationship between deep-fryer design, residence times at different temperatures, and oil composition. The half-lifetime of hydroperoxides (>15 min) is intermediate between vertical mixing times (<3 min) and longitudinal ones (>2 hours). Hydroperoxides of unsaturated fatty esters are generated at the surface, are preferentially decomposed in heated plumes and accumulate between production cycles in cold stagnant regions. Experimental validation is proposed for the eddy structure, temperature fluctuations, and hydroperoxides decomposition kinetics.

Keywords

Heat and mass transfer, oil oxidation, CFD, anisothermal oil flow, frying

I. Introduction

Deep-frying consists of immersing a food product in a liquid with a high boiling point liquid, usually a vegetable oil (denoted oil in the rest of the article). Oil is an ingredient incorporated within the finished product during cooking [1, 2] and the heat transfer fluid. Oil is a high Prandtl number fluid enabling intense heat transfer coefficients by natural convection (*i.e.*, in the vertical direction). As a result, fried products (French-fries, potato chips, chicken pieces and fingers, fish fillets, shrimp) are hot and crispy on the outside and cooked safely in the center (low risk of residual bacteria contamination). Due to the cycle of production of fried products in kitchen appliances, the residence time of oil within batch deep-fryers (several hours after repeated heating cycles) is much longer than frying time (indicatively from five to twenty minutes). Oil abuse by thermo-oxidation due to oxygen exposure at high temperatures can lead to various toxic compounds, with possible health concerns [3]. A similar matter exists for Maillard reactions with the apparition of carcinogenic acrylamide in contact with oil at high temperature [4]. Though no regulations have been established in the United States, the apparition of oxidation products is strongly regulated in the EU [5].

Vegetable oils are mixtures of triacylglycerols (TAG), which can be described as three fatty acids esterified onto the same glycerol backbone. Fatty esters (FE) naturally exhibit a variable number of carbon-carbon double bonds (unsaturations), which depend on plant variety [6]. Prevalent mono-, di-, and tri- unsaturated FE are the oleate (C18:1), linoleate (C18:2), and linolenate (C18:3). Unsaturated fatty esters are desirable in the diet with the following preference ratios 1:4:1 for FE with unsaturation in the $n-6$, $n-3$, $n-9$ position (also called $\omega-6$, $\omega-3$, $\omega-9$ FE), respectively [7, 8]. The positions are counted from the methyl end. These unsaturations are brought in common frying oils by linoleate ($n-6$), linolenate ($n-3$), and oleate ($n-9$), respectively. For example, these three fatty esters represent *ca.* 90% of FE in sunflower

oil. They are also the most sensitive to thermo-oxidation. The complex chemistry of thermo-oxidation leads to a dramatic loss of nutritional value by a displacement of double bonds (conjugated hydroperoxides), the apparition scission products (e.g., volatile aldehydes and esters [9]) responsible for off-flavors and toxic compounds (e.g., 4-HNE [3]), the production of cross-linked polymers responsible of fouling.

The first stages of the thermo-oxidation process are controlled by the kinetics of oxygen dissolution and intermediary products' transport through the oil bath [10, 11]. Similar effects have been shown in thermoplastics, where oxidation and polymer damages start from the external surfaces and the most exposed to atmospheric oxygen [12]. In simple words, mineral oxygen from the atmosphere is converted at the oil-air interface into chemically bounded oxygen (hydroperoxides). Hydroperoxides are thermally unstable products whose endothermic decomposition (*i.e.*, activated by increasing temperatures) generate either scission products (products responsible for the typical smell of fried products) or alkyl radicals, very reactive with oxygen. When the latter dominate, the oxidation process propagate in chain between the surface, the bulk, and the heating elements. In most of the EU member states, it is considered by law that frying oil should be discarded as soon as total polar compounds (TPC) exceed 25% in mass or a value similar. Polar compounds are defined as any species incorporating oxygen atoms beyond the initially present esters. Therefore, the legal oil lifetime depends on the rate of renewal of radicals responsible for the production of hydroperoxides and their subsequent decomposition in hot regions. As fried foods represent a significant fraction of the diet in Western and Asian countries, there is an urgent need to identify the possible strategies to minimize oil abuse and reduce oil wastes. Prior research focused on the reduction of oil uptake in fried products [1, 2]. While improving the dietary balance, this strategy reduces consumer exposure to oxidized products but does not explicitly address the loss of nutritional value in fried products. Little work has been done to relate the design of batch deep-fryers with oxidation

kinetics. Pioneer works [13, 14] in the sixties showed that substantial gain could be achieved by updating the surface-to-volume ratio of oil and oil flow distribution in the bath.

The current study addresses the lifetime hydroperoxides transported by the natural convection in the cavity of a kitchen appliance deep-fryer. We chose as reference a deep-fryer design including a cold zone below the submerged heating electrical resistor. Their decomposition is highly endothermic and is the root cause for all the inconveniences encountered during deep-frying: fouling, bad smells, reduced lifetimes, the apparition of toxic compounds. Coupling an anisothermal flow with a chemical reaction requires special treatment, as the molecular carrier is a TAG carrying different chemical functions with variable sensitivity to oxidation. This work shows as a Lagrangian description can reconcile the models based on mass balance on chemical functions and transport by an anisothermal flow.

The paper is organized as follows. Since deep-frying involves temperatures above the boiling point of pure water, section 2 justifies and details the oxidation model of edible oil between 80°C and 180°C and the formulation of hydroperoxide decomposition along streamlines. Our simulations cover the heating and holding periods, which is 50% to 90% of the deep-fryer's operation time. Indeed, the heat flux density between the oil and the frying product is so high (up to 150 kW·m⁻² [15, 16]) that a batch deep-fryer cannot operate a steady-state. Most of the operation time is used to recover the set temperature (maximum temperature 175°C according to [5]). The experimental conditions used to parameterize the hydroperoxides' decomposition model in isothermal conditions and to validate it in anisothermal ones are detailed in Section 3. Simulated results and the coupling between the transport and the degradation are analyzed in Section 4. Finally, the last section summarizes the main findings and the directions to keep oil healthy during deep-frying.

II. NUMERICAL METHODS

A. Combinatorial oxidation reaction kinetics

1. Principles

Triplet dioxygen is the common allotrope of oxygen in our environment. Because it carries two unpaired electrons, occupying two π molecular orbitals, it is a stable diradical, denoted $\text{^}\text{OO}\text{^}$ throughout the manuscript, as justified in Ref. [17]. Its unusual electronic structure explains why this abundant molecule is encouraged to react in the deep-fryer with an alkyl radical $\text{L}\text{^}$ centered on the carbon by forming bonds. Both radicals (di- and mono-) stabilize themselves, but the extra valence of dioxygen creates a new radical centered on oxygen, so-called peroxy radicals, and denoted $\text{LOO}\text{^}$. At this stage, it is crucial noticing that the abundant $\text{^}\text{OO}\text{^}$ diradicals cannot directly attack a fatty ester LH . The attack involves an intermediate step of hydrogen abstraction between $\text{LOO}\text{^}$ and LH (reaction R_{05} in Eq. (1)). This step between a radical and a stable species preserves free-valence and propagates it from oxygen to carbon atoms. The first oxidation products of fatty esters are hydroperoxides LOOH and radicals $\text{L}\text{^}$. In the context of deep-frying, the chain reaction's initiation occurs mainly by the continuous regeneration of $\text{L}\text{^}$ radicals at high temperatures [11]. Hydroperoxides are, indeed, unstable above 100°C [18] and decompose endothermically by homolytic scission of LO-OH bond (bond energy between 100 and $160\text{ kJ}\cdot\text{mol}^{-1}$) [19].

Bolland and Tobolsky [18, 20-22] pioneered the first general kinetic description of hydroperoxides in unsaturated materials (lipids, thermoplastic polymers). Depending on whether hydrogen bonds stabilize a cage mechanism (see Ref. [23]) or not, their decompositions are considered either unimolecular [24-35] or bimolecular [31, 33, 35, 36]. The molecularity of the decomposition remains an open question (see the discussion in Ref. [11]) in frying

conditions, but first-order decay has been mainly observed [24-26, 37-40]. In this work, unimolecular decomposition was chosen accordingly. The detailed mechanism reads [19, 30, 41]:

Eq. (1) is realistic, but it remains a simplified description of the full thermo-oxidation mechanism. It involves chemical functions and does not consider their carriers: either TAG or attached FE. Besides, the notation LH is ambiguous as it represents a generic unsaturated FE with several labile hydrogens, whose number and type depend on the considered FE. Labile hydrogens are in α position of a double bond (hold by the first carbon after the double bond). They are not equivalent as their abstraction energies vary from 313 $\text{kJ}\cdot\text{mol}^{-1}$ down to 209 $\text{kJ}\cdot\text{mol}^{-1}$ for mono- (*i.e.*, adjacent to one single unsaturated carbon atom) and bi-allylic (*i.e.*, adjacent to two unsaturated carbon atoms) hydrogen respectively [42]. The relative oxidability of C18:0 (stearate, no unsaturation), C18:1, C18:2 and C18:3 is ranked 1:11:114:179 [43]. Combining Eq. (1) and transport during deep-frying can be performed either by introducing a mass balance on the different types of labile protons and subsequent products or by introducing a mass balance on the different chemical functions held by the different unsaturated FE. Both balances are equivalent when the formation of di-, tri-, and cyclic hydroperoxides is discarded. This assumption was considered acceptable in the normal conditions of frying. Discarding FE

oxidized twice or three times facilitated the reconstruction of the profile of hydroperoxides from real experiments and the design of a thermal activation model.

Figure 1 summarizes the multiscale problem with the following key steps: the oil anisothermal flow, oxygen dissolution, transport of reactive species, and the desorption of scission products. At the scale of the oil tank, natural convection regularly exposes the oil to atmospheric dioxygen, where it is rapidly converted into hydroperoxides. Descending plumes remove hydroperoxides from the surface and spread them in the entire volume. As a result, a sharp oxygen density gradient is expected immediately below the oil-air surface. The detailed mechanism of how organic oxygen is transported and reacts within the oil volume remains unexplored, but with experimental arguments showing the speciation of termination reactions between the tank's top and bottom [10]. Coupling Eq. (1) with transport and temperature activation requires reasonable assumptions on carriers. Two stereospecific indices are needed to maintain the separability of carriers LH associated with labile hydrogens: a first one to designate glycerol derivatives' configuration (carbons 1-3 on the glycerol backbone) and another one to indicate the position of the dioxygen addition. Since the combinatory increases rapidly in real lipid mixtures, three approximation levels are suggested in Figure 1c. The coarsest description considers only oxygenated chemical species (hydroperoxide, alcohol, and carbonyl compounds). This choice prevails in the literature and neglects each FE or carrier site's specific reactivity. "Averaged" temperature activation models prevent reaction rates from being transposed from one deep-fryer to another or from oil to another. FE composition effects are recovered by considering either the oil as a mixture of FE or TAG. Replacing one single TAG by three independent FE (regardless of their branching on the glycerol backbone) in numerical models offers the best tradeoff between extrapolation capabilities and complexity. This level coarse-graining process was chosen in this study.

Figure 1: Coarse-grained description of the oxidation process at the scale of the deep-fryer. (a) a coarse-grained molecular description is proposed with building blocks between two to three heavy atoms. The plotted oxygen profile corresponds to the vertical density of oxygen atoms as calculated on the elementary volume. (b) Illustration of oxygen addition subsequently to a random abstraction of labile hydrogens (*i.e.*, on allylic sites). (c) Pro and cons associated with the loss of molecular details.

2. Coding the lineage of hydroperoxides

Hydroperoxides of FE, denoted LOOH, interact with native FE (*i.e.*, LH) in a statistical manner, leading rapidly to complex mixtures, with thousands of intermediates and final

oxidation products. The tracking of oxidation products is carried out by maintaining the original FE lineage and introducing prevalence assumptions. For the sake of simplicity, only unsaturated FEs were considered. Minor saturated FEs (laurate, palmitate, and stearate) were discarded because the abstraction energy of aliphatic hydrogens is much higher (418 kJ·mol⁻¹ [42]) than the allylic ones.

In this study, FE hydroperoxides were identified with triple indices, as $L_{i,j,k}$ OOH. All possible hydrogen abstraction cases and subsequent possible rearrangements from C18:1, C18:2, and C18:3 are shown in Table 1. The first index $i = 1, 2, 3$ identifies the FE carrier by its number of unsaturations (*e.g.*, $i = 2$ codes for C18:2). For the same FE carrier, possible hydroperoxides differ from the position of the hydroperoxide function (OOH) and the configuration of the substituent groups (*cis* or *trans*, see [44-46]). j is the isomer index in the delta nomenclature system [47] and k the stereoisomer index. In shorts, 8, 4, and 4 different hydroperoxides can be produced from $i = 1, 2, 3$ respectively. It is worth noticing that the proposed coarse-graining reduced the complexity dramatically to consider. In the real-life, each TAG carries 0 to 3 hydroperoxide functions, evolving to one of the $\left((8+1)+2 \times (4+1)\right)^3 - \left((8+1)+2 \times (4+1)\right)^2 = 6498$ non-palindromic sequences of hydroperoxides. Each of them may exhibit potentially different stabilities with temperature.

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Table 1: Structure of initial fatty esters and hydroperoxides produced by autoxidation and proportion of each isomers at a specific temperature. Empty and filled arrows indicated the position of mono-allylic and bi-allylic hydrogens, respectively.

Fatty ester	Fatty ester structure [†]	Hydroperoxide isomers	Hydroperoxide structure	i	j	k	Prevalence 100×(kg _{isomers} / kg _{LOOH})	Refs.	
Oleate (<i>cis</i>)		trans-9-OOH		1	1	2	22.5	45	
		trans-10-OOH		1	2	2	22		
		trans-8-OOH		1	3	2	19.5		
		trans-11-OOH		1	4	2	19		
		cis-8-OOH		1	3	1	5.4		
		cis-11-OOH		1	4	1	6.1		
		cis-10-OOH		1	2	1	2.8		
		cis-9-OOH		1	1	1	2.7		
Linoleate (<i>cis-cis</i>)		trans-trans-9-OOH		2	1	2	90	46	
		trans-trans-13-OOH		2	2	2			
		cis-trans-9-OOH		2	1	1	10		
		cis-trans-13-OOH		2	2	1			
Linolenate (<i>cis-cis-cis</i>)		cis-cis-trans-16-OOH		3	1	2	43.3	44	
		trans-cis-cis-9-OOH		3	2	2	34.2		
		cis-trans-cis-13-OOH		3	1	1	11.5		
		cis-trans-cis-12-OOH		3	2	1	11		

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[45]: autoxidation at 95°C, [46]: autoxidation at 75°C, [44]: autoxidation at 80°C. [†]Roman numbers represent the carbon numbers according to the delta nomenclature system [47].

218

The proposed coarse-graining level recasts Eq. (1) into four populations of FE, denoted

$\{i_1, j_1, k_1\}, \{i_2, j_2, k_2\}, \{i_3, j_3, k_3\}, \{i_4, j_4, k_4\} :$

The combinatorial description propagates the lineage iteratively from initial FE to subsequent products. Reaction rates constants $k_{d_{i,j,k}}$ and $k_{p_{i,j,k}}$ need to be identified from carefully chosen experiments, accounting for the thermal stability of each considered hydroperoxide [48] and the lability of hydrogens in considered unoxidized FE [49]. Though TAG carriers were discarded in the model, preserving FE enables direct comparison with experiments with pure FE, pure oils (TAG mixtures), and oil blends.

B. 3D unsteady CFD simulations of turbulent natural convection in a batch deep-fryer

1. Governing equations

The buoyancy-driven oil flow in the deep-fryer was simulated under the Boussinesq approximation by assuming a constant isobaric thermal expansion coefficient:

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \tag{3}$$

235 where ρ is the oil density and T is the oil temperature.

236 The equations of continuity, momentum, and energy are:

$$\begin{aligned}
 &\nabla \cdot \mathbf{v} = 0 \\
 237 \quad &\rho \left[\frac{\partial \mathbf{v}}{\partial t} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right] = \nabla \cdot (\mu \nabla \mathbf{v}) - \nabla p + \rho [1 - \beta(T - T_0)] \mathbf{g} \quad (4) \\
 &\rho C_p \frac{dT}{dt} = \nabla \cdot (k \nabla T)
 \end{aligned}$$

238 where $\mathbf{v}$, p and T are the velocity, pressure, and temperature fields, respectively. The

239 dynamic viscosity, μ , the heat capacity, C_p , and the thermal conductivity, λ , were allowed to

240 vary with temperature as tabulated in Table 1. $\mathbf{g}$ is the gravitational acceleration.

241

242 **Figure 2. Design of the reference deep-fryer used in this study: (a) overview of the deep-fryer equipped with three**
 243 **windows to image the flow, (b) top view of the tank, (c-d) overview of the mesh. Positions indicated by 1, 2, 3 and 4 in**
 244 **blue circles correspond to the center ($X=0, Y=0, Z=0$), the top($X=0, Y=0, Z=0.0514$ m), the lateral ($X=0.08, Y=0, Z=0$)**
 245 **and the bottom ($X=0, Y=0, Z=-0.041$ m) respectively.**

246 No-slip was set for the flow at all boundaries:

$$247 \quad \mathbf{v} = 0 \quad (5)$$

248 At the walls of the tank (1.2 mm thick stainless steel for the vertical walls) $\partial\Omega_2$ and in
249 agreement with temperature and flux measurements, an effective heat loss by conduction,
250 convection, and radiation (linearized temperature dependence) was applied:

$$251 \quad -\mathbf{n}|_{\partial\Omega_2} \cdot \lambda \nabla T = h_2 (T - T_\infty) \quad (6)$$

252 At the free surface with air ($\partial\Omega_1$), a slip boundary condition was applied. Erasing the vertical
253 component of velocity is an acceptable approximation, but, in the real-life, heating plumes at
254 the vertical of the heating elements make the surface rough and turbulent even in the absence
255 of food products. These effects increase the oil surface area exposed to air, and therefore
256 oxygen. A heat loss by convection was enforced at the free surface. Eqs. (6) and (8) assuming
257 that the surrounding temperature, T_∞ , is kept at 25°C.

$$258 \quad -\mathbf{n}|_{\partial\Omega_1} \cdot \mathbf{v} = 0, \quad -\mathbf{t}|_{\partial\Omega_1} \cdot [-\nabla p + \nabla \cdot (\mu \nabla \mathbf{v})] \mathbf{n}|_{\partial\Omega_1} = 0 \quad (7)$$

$$259 \quad -\mathbf{n}|_{\partial\Omega_1} \cdot \lambda \nabla T = h_1 (T - T_\infty) \quad (8)$$

260 Heat is transferred to oil via a three-coil sheathed tubular heating element (heating surface area:
261 $2.23 \cdot 10^{-2} \text{ m}^2$) placed above the tank's bottom. Two bulb and capillary thermostats placed in the
262 middle of the first coil control temperature, as shown in Figure 2a. The longest and thinnest
263 bulb positioned near the heating element's bottom plane prevents oil overheating above 200-
264 210°C. The second bulb is positioned at the mid-height of the heating element and controls the
265 frying temperature. Although very basic, the second sensor's mechanical thermostat offers a
266 somewhat frequency proportional control close to the set temperature. The heating periods are

267 long, far from the setpoint, and shorter otherwise. A similar on-off control was implemented
 268 numerically by imposing the heat flux, Φ_3 , at the external wall of the tubular heating element
 269 (effective heat flux density $\phi_3 = 9.2 \cdot 10^4 \text{ W} \cdot \text{m}^{-2}$). The skin temperature of the heating element,
 270 T_{skin} , was given by:

$$271 \quad -\mathbf{n}|_{\partial\Omega_3} \cdot \Phi_3^{(t)} = h_3 (T_{skin} - T) \quad (9)$$

with $\Phi_3 = 0$ when $T_{frying} > T_{set}$, $\Phi_3 = \phi_3$ otherwise

272 The frying temperature T_{frying} was defined by frying temperature at position 1 (see Figure 2
 273 X=0, Y=0, Z=0). The set temperature T_{set} was chosen equal to 165°C. In the real and simulated
 274 oil baths, the skin temperature reached values up to 40°C above T_{frying} . All simulations started
 275 with an initial temperature of 25°C equal to the ambient one T_∞ .

276 **Table 2. List of parameters used to simulate the anisothermal heat flow within the deep-fryer.**

Parameters	Symbols	Value	Units	Refs.
<i>sunflower oil</i>				
density	ρ	$\rho(T) = -0.64T + 1101.1$ with T in K	$kg \cdot m^{-3}$	[50]
thermal expansion coefficient	β	$7.0 \cdot 10^{-4}$	K^{-1}	-
dynamic viscosity	μ	$\mu(T) = 4.37 \cdot 10^{-6} \exp\left(-\frac{23.4 \cdot 10^{-6}}{RT}\right)$ with T in K	$Pa \cdot s$	[51]
specific heat capacity	C_p	$C_p(T) = 3.477 \cdot 10^{-3} (T - 273.15) + 2.566$ with T in K	$kJ \cdot kg^{-1} \cdot K^{-1}$	[51]
thermal conductivity	k	$k(T) = 0.149 + 10^{-4}T$ with T in K	$W \cdot m^{-1} \cdot K^{-1}$	[52]
<i>deep-fryer (technical specifications)</i>				
oil tank length	L_e	$26.51 \cdot 10^{-2}$	m	-
oil tank width	W	$17.82 \cdot 10^{-2}$	m	-
oil height	H	$9.14 \cdot 10^{-2}$	m	-
oil volume	V_{oil}	4	L	-
oil initial temperature	T_0	25	°C	-

oil set temperature	T_{frying}	165	°C	-
maximum power of the heating element	P_{max}	2000	W	-
convective heat transfer coefficients (validated experimentally at steady state, >9 min after initial heating)				
free surface	h_1	8 from the correlation $Nu_L = 0.14Ra_L^{1/3}$ with $L = W$	$W \cdot m^{-2} K^{-1}$	[53]
walls	h_2	2 (experimental determination)	$W \cdot m^{-2} K^{-1}$	-
heating element	h_3	from the correlation $Nu_L = 0.145Ra_L^{0.29}$ with $L = 0.07$ m (oil height above the heating element)	$W \cdot m^{-2} K^{-1}$	[54, 55]

277 where $Nu_L = \frac{h_i L}{\lambda}$ for $i = 1, 3$, $Ra = \frac{g \beta \Delta T L^3}{(\mu / \rho)^2 \text{Pr}}$ and $\text{Pr} = \frac{\mu C_p}{k}$ are Nusselt, Rayleigh and

278 Prandtl dimensionless numbers, respectively.

279

280 2. Numerical resolution

281 Eq. (3)-(9) were resolved in time and space numerically with the CFD software Ansys-Fluent
282 (version 17, Ansys, USA). Velocity and temperature fields inside the tank were simulated
283 during the first 10-12 minutes of heating until an apparent steady-state was observed in the
284 region above the heating element. Ansys-Gambit (version 2.4.6) has been used for mesh
285 generation and applied to deep-fryer sketched in 3D with an accuracy of ± 0.2 mm. The mesh
286 validation study showed an optimal mesh consisting of 637 186 tetrahedral cells for the entire
287 oil bath, with the finest mesh size chosen as $\delta_{\min} = \min\left(\frac{L}{2Nu_L}\right) \sim 1.5$ mm [55] to capture thermal
288 and dynamic boundary layer effects near cold and hot surfaces. The Nusselt number imposed
289 the minimal thickness at the heating elements (where L is the external diameter of the heating
290 element).

291 The second-order SIMPLE scheme (Semi Implicit Method for Pressure Linked Equations) was
292 used to integrate the pressure-velocity equations in time. Simulations were run up to 2×10^4 time

293 steps with a fixed time step size chosen as $\Delta t = \frac{\Delta x_{min}}{v_{max}} = 0.0542$ s. $\Delta x_{min} = 2$ mm was chosen
 294 slightly larger than the finest cell's size at the vicinity of the heating element. The maximum
 295 velocity was estimated conservatively as $v_{max} = 1.05 \frac{\lambda}{\rho L C_p} Ra_L^{0.43} Pr^{1/3}$ by fitting the maximum
 296 turbulent velocity determined experimentally in a Rayleigh-Bénard water tank for an equivalent
 297 $Ra \sim 10^7$ [55]. It was previously verified on this equivalent configuration that the turbulence
 298 treatment would not require Direct Numerical Simulation (DNS). LES (Large-Eddy
 299 Simulation) was, therefore, applied for this study. Unresolved small-scale details, particularly
 300 the transported temperature-field near boundaries, were estimated with the Smagorinsky-Lilly
 301 subgrid-scale model acting as a low-pass filter.

302 C. *Hydroperoxide decomposition model along streamlines*

303 Figure 1 illustrates the likely coupling between the transport of chemical species after exposure
 304 to atmospheric oxygen in regions with different temperatures. This study focuses on the thermal
 305 decomposition of $L_{i,j,k}OOH$ considering that they are produced from the top surface, and they
 306 are subsequently dispersed by the flow in the bulk volume, including beneath the heating
 307 element. The residence time of hydroperoxides away from the surface limits the effective
 308 thermo-oxidation rate when the propagation rate is close to the decomposition rate of
 309 $L_{i,j,k}OOH$ (*i.e.*, reaction chain length close to unity). This condition is identified on the
 310 oxidation kinetics by a concentration maximum in total hydroperoxides (*i.e.*, they are renewed
 311 as fast they are decomposed. A detailed map of residence times was required to evaluate the
 312 lifetimes of $L_{i,j,k}OOH$ in the presence of large oil temperature heterogeneities (*i.e.*, up to 80°C).
 313 Eulerian descriptions of decomposition kinetics were not favored as they do not offer direct
 314 relationships between residence times and recirculation loops. Comparatively, Lagrangian

descriptions can deal efficiently with any source (point, surface, and volume) and are straightforward to implement for unimolecular reactions (first-order).

The variation of hydroperoxide concentration of a fluid particle p along the streamline $\mathbb{S}_p$ equipped with the curvilinear coordinate ℓ corresponding to the cartesian coordinates (x, y, z) depends on the local residence time $\mathbf{U}|_{x,y,z} \cdot \boldsymbol{\theta}|_{\ell}^{\mathbb{S}_p}$ and the local temperature $T|_{x,y,z}$. The unimolecular hydroperoxide decomposition along $\mathbb{S}_p$ reads:

$$\begin{aligned} \frac{d[\text{L}_{i,j,k}\text{OOH}]}{d\ell}\bigg|_{\ell}^{\mathbb{S}_p} &= \frac{d[\text{L}_{i,j,k}\text{OOH}]}{dt}\bigg|_{\ell}^{\mathbb{S}_p} \frac{dt}{d\ell}\bigg|_{\ell}^{\mathbb{S}_p} \\ &= -k_{d_{i,j,k}}(T|_{x,y,z})[\text{L}_{i,j,k}\text{OOH}]_{\ell}^{\mathbb{S}_p} \frac{1}{\mathbf{U}|_{x,y,z} \cdot \boldsymbol{\theta}|_{\ell}^{\mathbb{S}_p}} \end{aligned} \quad (10)$$

where $\mathbf{U}|_{x,y,z}$ is the local velocity vector oil and $\boldsymbol{\theta}|_{\ell}^{\mathbb{S}_p}$ is the unitary vector tangent to the streamline $\mathbb{S}_p$.

In anoxia conditions (*i.e.*, without hydroperoxide regeneration), the local concentration in any location of the deep-fryer is obtained by averaging the decomposition over a representative set of trajectories starting from a reference region (*e.g.*, surface) and joined in the same point (x, y, z) . By denoting $\{\ell_{x,y,z}^{\mathbb{S}_p}\}_{p=1..N}$ the lengths of the N trajectories in the set, the variation of hydroperoxide content becomes for an arbitrary initial distribution of hydroperoxides:

$$[\text{L}_{i,j,k}\text{OOH}]_{x,y,z} = \left\langle [\text{L}_{i,j,k}\text{OOH}]_{\text{initial}}^{\mathbb{S}_p} \right\rangle - \left\langle \int_0^{\ell_{x,y,z}^{\mathbb{S}_p}} \frac{d[\text{L}_{i,j,k}\text{OOH}]}{d\ell}\bigg|_{\ell}^{\mathbb{S}_p} d\ell \right\rangle \quad (11)$$

where $\langle X \rangle$ is the mean of X along N trajectories.

331 By noticing that $\frac{d \ln[L_{i,j,k} \text{OOH}]}{d\ell} \Big|_{\ell}^{\mathbb{N}_p} = -\frac{k_{d_{i,j,k}}(T|_{x,y,z})}{\mathbf{U}|_{x,y,z} \cdot \boldsymbol{\theta}|_{\ell}^{\mathbb{N}_p}}$ for first-order kinetics, the variation of
 332 hydroperoxide content is also related to the distribution of residence times at different
 333 temperatures for considered trajectories:

$$\begin{aligned}
 334 \quad \ln \left(\frac{[L_{i,j,k} \text{OOH}]|_{x,y,z}}{\langle [L_{i,j,k} \text{OOH}]|_{\text{initial}}^{\mathbb{N}_p} \rangle} \right) &= \left\langle \int_0^{\mathbb{N}_p} \frac{d \ln[L_{i,j,k} \text{OOH}]}{d\ell} \Big|_{\ell} dl \right\rangle = - \left\langle \int_0^{\mathbb{N}_p} \frac{k_{d_{i,j,k}}(T|_{x,y,z})}{\mathbf{U}|_{x,y,z} \cdot \boldsymbol{\theta}|_{\ell}^{\mathbb{N}_p}} dl \right\rangle \\
 &\approx \sum_{q=1..N_T} k_{d_{i,j,k}}(T_q) \langle \tau_{T_q} \rangle
 \end{aligned} \quad (12)$$

335 where $\langle \tau_{T_q} \rangle$ is the averaged residence time at temperature T_q with $q = 1 \dots N_T$; N_T is the number
 336 classes uses to discretizes the considered temperature range.

337 D. Validation of an activation model for the decomposition of $L_{i,j,k} \text{OOH}$ in 338 mixtures in isothermal conditions

339 According to Table 1 and Eq. (2), sixteen different hydroperoxides may be decomposed
 340 according to sixteen different rate constants. All individual values cannot be determined
 341 experimentally because the different $L_{i,j,k} \text{OOH}$ cannot be produced independently, even from a
 342 pure FE. Reconstructing their concentrations from TAG or FE initial composition is an option
 343 but at the expense of adding unknown production or renewal rates.

344 A feasible approach was followed by tracking only the likeliest hydroperoxide isomers of each
 345 FE, as supported by qualitative experiments on pure FE. Since hydroperoxides from oleate,
 346 linoleate, and linolenate exhibit different thermal stability [48, 56], the index i was kept.
 347 Among stereoisomers, trans-hydroperoxides, conjugated or not, are more stable and prevail at
 348 high temperatures, so that only the case $k = 2$ was considered. For instance, 83% of *trans* oleate
 349 hydroperoxides are present at 95°C, and 90% of conjugated trans-trans linoleate

hydroperoxides are present at 75°C. Additionally, since isomers 13-OOH and 9-OOH hydroperoxides of linoleate have similar lifetimes at high temperatures [57], the proposed mass balance did not separate them (or $j = 2$), and the less probable isomer 11-OOH was neglected (see the justification in Ref. [58]). As a result, indices j and k were dropped and $L_i\text{OOH}$ represented the likeliest mixture of $L_{i,j=1 \text{ or } 2, k=2}\text{OOH}$, with $i = 1, 2, 3$.

The rationale for the transposition of constant rates from pure FE to complex TAG mixtures (with 3 FE attached to glycerol) was tested on two oils from 40 to 120°C: poppyseed (13% oleate, 75% linoleate, and 0.6% linolenate, from Ref. [59]) and linseed (22% oleate, 13% linoleate and 54% linolenate, from Ref. [60]). All oxidation kinetics were obtained in isothermal conditions under mechanical mixing. Reported experimental peroxide values, expressed in milli-equivalents peroxide or O_2 per 1 kg of fat (see interpretation **Figure 1c**), were related to the total amount of hydroperoxides (*i.e.*, regardless of the FE or TAG carrier) as:

$$[\text{LOOH}]_{\text{total}}^{(t)} = \sum_{i=1}^3 [L_i\text{OOH}]^{(t)} \quad (13)$$

Since hydroperoxides were obtained during or after oxygen exposure, the corresponding $[L_i\text{OOH}]$ kinetics were reconstructed from $[\text{LOOH}]_{\text{total}}^{(t)}$ ones using a simplified version of Eqs. (2), as detailed in Appendix A. Typical reconstructed kinetics during the decomposition-dominant phase are shown in Figure 3. Aerated and anoxia conditions reproduced those encountered at the surface and in the oil bulk volume without temperature gradient. Decomposition rate constants, k_{d_i} , were read from Figure 4. Propagation rate constants k_{p_1} and k_{p_2} were fitted from experimental data in the presence of oxygen (no fitting required in anoxia) [61]. Predictions were highly acceptable at 80°C and above, *i.e.* in the frying temperature range. At 40°C, the time to reach a steady-state (maximum of $[\text{LOOH}]_{\text{total}}^{(t)}$) was underestimated, and

372 the effective decomposition rate was overestimated (see Figure 3e-f). At ambient temperatures,
373 hydroperoxides' stabilization by hydrogen bonds would favor bimolecular decompositions
374 (cage-effect mechanism) instead of unimolecular ones.

375 The preliminary validation in isothermal conditions generalized to mixtures oxidation schemes
376 proposed for thin films or homogeneous conditions (see Ref. [61]). The remainder of the study
377 will extrapolate previous results from isothermal to anisothermal conditions by introducing an
378 activation energy for the decomposition of each L_iOOH . As the corresponding activation
379 entropies capture the decomposition's molecularity, only reference kinetics above 80°C were
380 subsequently considered.

Figure 3: Comparison between predicted (lines) and experimental (symbols) kinetics of total hydroperoxide content in oxygenated conditions (filled symbols) and in anoxia (empty symbols). Experimental data in poppyseed oil (PO) and linseed oil (LO) are from Ref. [61]. The different subpopulations of hydroperoxides are presented in the inlets. When index i has been dropped, the value represents the total concentration in hydroperoxides.

386

387 **III. EXPERIMENTAL METHODS**

388 **A. *Oil and fatty acid methyl esters***

389 Fresh sunflower oil (SO) was supplied directly by the Lesieur's refinery production plant of
390 Coudekerque (France). Methyl oleate (Alda Aesar, purity of 96%), methyl linoleate (Acros
391 Organics, purity of 99%), and methyl linolenate (Sigma Aldrich, purity of 99%) were
392 purchased.

393 **B. *Deep-fryer***

394 The reference deep-fryer used in this study was a commercial kitchen appliance (model Semi-
395 Pro, SEB, France, oil capacity 4 L, 2052W) including an immersed heating element (surface
396 area: 222.7 cm²). A second deep-fryer with an alternative design was also considered to
397 highlight the effect of design on the decomposition of hydroperoxides and indirectly on oil
398 lifetime.

399 **C. *Bubbling reactor***

400 Reaction rates of hydroperoxide decomposition of pure FE were determined in a miniaturized
401 bubbling reactor (vertical tube reactor of capacity 30 mL), based on the principles as the larger
402 one described in Ref [11]. The FE temperature was controlled by immersing the glass reactor
403 within a large secondary oil bath (0.5 L, heating power 600 W) equipped with a PID
404 temperature-controller. Dry air or nitrogen was injected from the bottom of the test tube with
405 the help of a Pasteur pipette to reproduce aerated or anoxia conditions, respectively.

D. *Determination of hydroperoxide content*

The total hydroperoxide content was determined experimentally by differential scanning calorimetry (DSC) according to the method described in Ref. [62]. A small oil aliquot (10-20 mg) was heated from 25°C to 250°C at a rate of 3°C/min. Since the endothermic decomposition of hydroperoxides in the pan occurs in anoxia, the formed radicals recombine together exothermically into stable products. The total amount of hydroperoxides was quantified by assuming an effective enthalpy of decomposition of 320 kJ/mol.

E. *Temperature measurements*

Local temperatures in the oil bath were recorded with thermocouples (type K, TC SA, France) connected to a data acquisition system (Ni cDAQ-9178 and module NI 9213, National Instruments, Austin, Texas, USA) at a frequency of 3 Hz. Temperatures at the surface of the oil bath were imaged with a thermal camera (model Ti9, Fluke, USA) with a emissivity of 0.95.

IV. Results and Discussion

A. *Parametrization of the hydroperoxide decomposition kinetic model*

The assumption of first-order decomposition kinetic of all L_iOOH was tested on pure FEs, including seven kinetics of oleate hydroperoxide (ranging from 80°C and 180°C), five kinetics of linoleate hydroperoxides (ranging from 120°C to 180°C), and seven kinetics of linolenate hydroperoxides (ranging from 100°C to 180°C). Decompositions were monitored in the bubbling reactor in strict anoxia. Normalized kinetics are shown as semi-log plots in Figure 4a-c with corresponding Arrhenius plots depicted in Figure 4d along with reaction rates reported in the literature. All linearized plots confirmed unimolecular decomposition in frying conditions. Strong activation of decomposition by temperature was evidenced for all hydroperoxides with a lifetime reduction varying from 50 to 400 from 80°C to 180°C. Oleate

429 hydroperoxides exhibited the highest stability with temperature and the highest activation
 430 energy around $78 \text{ kJ}\cdot\text{mol}^{-1}$.

432 **Figure 4. Kinetics of decomposition of hydroperoxides of pure esters (a) methyl oleate (MO), (b) methyl linoleate (ML),**
 433 **(c) methyl linolenate (MLn) in frying conditions, and (d) their corresponding decomposition rate constants and**
 434 **activation energies. Empty symbols are from literature: A from Ref. [38] (ethyl oleate), B from Ref. [39] (MO), C from**
 435 **Ref. [40], E from Ref. [63], F from Ref. [26], G from Ref. [25], H from Ref. [64], I from Ref. [65], J from Ref. [24] and**
 436 **K from Ref. [66]. Filled symbols are from this work and produced in anoxia (nitrogen flow rate of $0.5 \text{ L}\cdot\text{min}^{-1}$) in the**
 437 **bubbling reactor.**

438

439 Decomposition rate constants were fitted with an Arrhenian activation model:

440
$$k_{d_i}(T) = k_i^0 \exp\left(\frac{-Ea_i}{RT}\right) \text{ with } i=1,2,3 \quad (14)$$

441 where k_i^0 is the pre-exponential factor, Ea_i the activation energy, R the gas constant, and T is
442 absolute temperature. The distributions of activation energies and pre-exponential factors due
443 to uncertainties were estimated by bootstrap (1000 samples). It was particularly noticeable that
444 all hydroperoxides' decomposition rates looked similar at 180°C whereas they were different
445 at 80°C. It is, therefore, hinted that all FE hydroperoxides propagate oxidation at the highest
446 frying temperature, whereas only the most labile ones do during initial heating.

447 B. *CFD results*

448 1. *Validation during the initial heating period*

449 Simulated 3D temperature and velocity fields during the heating step were recorded with a
450 temporal resolution of ~54 s. They are plotted along three principal planes of the deep-fryer in
451 Figure 5. Along the smallest vertical cross-section XZ, the four heating element branches
452 generate four ascensional plumes starting as shown at t=54s. Two convections cells are fully
453 developed after one min and are maintained throughout the whole heating period (up to 542 s).
454 The circulation operates mainly within the plane XZ without a significant mixing in the plane
455 YZ. The ascensional sections are small and associated with ascensional velocities up to 2.8
456 cm·s⁻¹. Descent regions are located along the walls are thicker with velocities up to 4 mm·s⁻¹
457 The region below the heating element remains stagnant with delayed heating.

458

Figure 5: Temperature and velocity distributions during initial heating in three principal planes of the deep fryer

Measured temperature kinetics and surface temperatures are shown in Figure 6. Simulated temperatures at the center-of-mass and 20 mm below the heating element are also given. They were in good agreement. Measured surface temperatures confirmed hot spots aligned with elements coils, but each of them separated by 3 to 4 cm. Surface temperatures were heterogeneous, with variations reaching up to 15-20°C while continuous heating was applied.

Once the set temperature was reached after ca. 9 min, surface heterogeneities decreased down to 5°C. During 10 min of simulation, steady-state (flow and temperature) was reached above the heating element, but it would have required 2 hours to reach steady-state below the heating element.

Figure 6. a) Thermal imaging of the oil bath surface during the heating period and b) the corresponding temperature distribution and c) the comparison between measured (continuous lines) and simulated (symbols) local temperature.

Simulation's consistency was evaluated by plotting in Figure 7 the temperature z -profile along the bath's centreline. Profile details near the free surface (Figure 7b) show a ca. 3 mm thick boundary layer, that matches the thermal boundary layer simulated from DNS calculations with $Ra_L^{-0.291}$ [67, 68].

Figure 7: a) Kinetics of temperature profile along Z during heating and b) zoom near the surface region

2. Analysis of the turbulence

Oil flew as smooth plumes at the vertical of the heating coils before spreading in multiple whorls and eddies. Large-scale turbulent patterns were visually revealed by the change of the refraction index and the displacements of solid particles (see, for example, Figure 9b). The flow was asymmetrically structured between ascending and descending flows. Hot plumes rose rapidly in an almost laminar fashion before spreading rapidly along the shortest cross-section. The descent was conversely more turbulent and dissipated progressively in the entire volume. Turbulence on small scales was analyzed in Figure 8 from the temporal fluctuations of velocities and temperatures at four typical positions in the deep-fryer (reported in Figure 2). Although the entire system was out of equilibrium during heating, velocity fluctuations were thought ergodic enough on short and intermediate length scales so that Taylor's hypothesis of

frozen turbulence held. Normalized spectra of velocity autovariance are plotted vs. natural frequency, f in Figure 8a. Its interpretation within the Kolmogorov turbulence phenomenology requires to relate temporal fluctuations with spatial ones. By assuming that the convected eddy pasts the probe with a mean convection velocity U and unchanged characteristics, the frozen turbulence assumption associates the wavelength L/n with $f = nU/L$. L represents the largest length scale and n any number greater than 1. All Power spectra were similar and exhibited power-law decays as f^{-m} with exponents $m \approx 5/3$ at intermediate frequencies ranging from 0.4 and 8 Hz. Spectra invariant with position and 5/3's scaling signed locally isotropic turbulence in the inertial subrange, where turbulent kinetic energies cascaded from production scales (low frequencies) down to dissipation scales (high frequencies) [69]. This result, never shown in a deep-fryer, suggests an efficient mixing down to the millimeter scale within the deep-fryer due to turbulence. On intermediate time scales, the power spectra of temperature fluctuations decreased rapidly with f , but not isotropically or in a self-similar manner. Simulated and measured spectra were quite similar and were approximately associated with an exponent $m \approx 7/5$, in agreement with stratified turbulence [70, 71] The stratification was exemplified by fluctuations of velocities and temperatures three magnitude orders lower below the heating element (bottom position).

The flow described with a deep-fryer under constant heating differed from the classic configuration of Rayleigh-Bénard natural convection cells [68, 72]. In particular, fluctuations did not decrease at the vicinity of the free surface and did not increase at the deep-fryer center. The differences arose from the heating element's geometry covering only a small fraction of the deep-fryer's bottom, the heat loss at the surface. The presence of a cold zone but not isothermal below the heating element also affected the gap between the vertical walls and the heating element. The contribution of heating on temperature fluctuations at the centre of the deep-fryer were analysed by plotting the windowed mean square of experimental fluctuations

517 at different time scales, $\tau = 1/f$, in Figure 8c. The passage of plumes is visible on short time
518 scales with an external envelope decreasing exponentially according to two times scales: 28 s
519 and 127 s. The fastest decay was associated with the oscillations of plumes and the longest to
520 vertical mixing. Fluctuations were lower than $\pm 2.1^{\circ}\text{C}$ at steady state and were independent τ
521 .
522

Figure 8. Analyses of fluctuations of (a) velocities and (b-c) temperatures. PSD. (a-b) Temporal power spectrum densities at different positions and comparison with its scaling as f^{-m} with $m = 5/3$ for isotropic scaling [69] and $m = 7/5$ for stratified scaling [70]. (c) Windowed mean-square fluctuations as measured at the center of the deep-fryer (τ is the width of the window).

C. Description of oil flow at steady state

At steady state, the natural convection is fully developed in the entire oil bath, as shown in Figure 9. The spatial distribution of residence times was estimated on a regular grid of elementary volumes V_r from mass flow considering a compressible flow according to the following equation:

$$t_r(x, y, z) = \frac{\int_{V_r} \rho(x, y, z) dx dy dz}{\sum_{f=1..6} \int_{\partial\Omega_f} (\rho(x, y, z) \mathbf{U}(x, y, z) \cdot \mathbf{n}_{\partial\Omega_f}) H[\mathbf{U}(x, y, z) \cdot \mathbf{n}_{\partial\Omega_f}] d\Omega_f} \quad (15)$$

where $\mathbf{U}(x, y, z)$ is the velocity field at positions (x, y, z) , $\rho(x, y, z)$ is the oil density at the same positions calculated from the local temperature. $\{\partial\Omega_f\}_{f=1..6}$ are the faces of the element with normals $\mathbf{n}_{\partial\Omega_f}$ and H the Heaviside function.

Local residence times shown in Figure 9a were calculated with a spatial resolution of 1.7 mm. They highlighted the presence of a central chimney where oil transited rapidly. Its presence was confirmed by the direct observation of the flow (Figure 9b). The tracked particle shows that the chimney compartmented recirculation loops on both sides of the cross section. Dwelling times below the heating element reaches several minutes up to almost one hour with temperatures 80°C lower than those observed above. As first approximation and in agreement with the overrepresentation of cold surfaces, residence times were significantly greater in cold regions than in cold ones. Non-uniform residence times correlated with non-uniform temperature distributions would extend the lifetime of hydroperoxides and confirmed our initial intuition about the likely relationship between deep-fryer design and oil abuse.

Figure 9. (a) Temperature (iso-contours), velocity (arrows) and residence time (color) fields at steady state in the principal planes of the deep-fryer (resolution of 1.7 mm) and (b) experimental observations of scattered light at 90° through the plane XZ at steady state. The amount of scattered light characterized temperature gradients and the presence advected particles (~ 20 flat wood chip particles with a diameter of ca. 3-5 mm were dispersed in oil bath). The red circle tracks the position of these particles. (c.) Residence time at different temperatures of two trajectories in the bottom and in the top region.

D. *Coupling between anisothermal oil flow, transport and hydroperoxide decomposition in the deep-fryer*

The transport of hydroperoxides from one region to another one was simulated at steady state using a Lagrangian formulation. This description enables to simulate transport on time scales (several hours) much longer than those use to simulate the flow velocity at steady state ($\mathbf{U}|_{x,y,z}^{steady}$). The trajectory of fluid particle “ α ” containing hydroperoxides was integrated explicitly over time, where the displacement $\Delta \mathbf{r}_\alpha$ during Δt is given by:

$$\Delta \mathbf{r}_\alpha|_{x,y,z} = \mathbf{U}|_{x,y,z}^{steady} \Delta t + \sqrt{\langle \Delta \tilde{\mathbf{r}}_\alpha^2|_{x,y,z} \rangle} \underline{\underline{\mathbf{N}}}(\mathbf{0}, \mathbf{1}) \quad (16)$$

where $\underline{\underline{\mathbf{N}}}(\mathbf{0}, \mathbf{1})$ is a 3×3 diagonal matrix whose diagonal elements are random drawn from the standard normal distribution. $\langle \Delta \tilde{\mathbf{r}}_\alpha^2|_{x,y,z} \rangle$ is the mean-square displacement due to the random contribution of turbulence, where angular brackets denote an ensemble average.

Following Taylor’s theory, fluctuations of particle velocities were assumed to be governed by a stationary random process so that $\langle \Delta \tilde{\mathbf{r}}_\alpha^2|_{x,y,z} \rangle$ could be estimated from their local autocorrelation function $\rho_\alpha^2|_{x,y,z}(\tau)$ depending on lag τ but not on time t . From Eq. 12.148 of Ref. [73] it reads:

$$\langle \Delta \tilde{\mathbf{r}}_\alpha^2|_{x,y,z} \rangle = 2 \langle \mathbf{u}|_{x,y,z}^2 \rangle \Delta t \int_0^{\Delta t} \left(1 - \frac{\tau}{\Delta t}\right) \rho_\alpha^2|_{x,y,z}(\tau) d\tau \quad (17)$$

574 where $\langle \mathbf{u}|_{x,y,z}^2 \rangle$ is the variance of fluctuations. By choosing an integration time step sufficiently

575 small comparatively to the total correlation time $\Lambda|_{x,y,z} = \int_0^{+\infty} \rho_\alpha^2|_{x,y,z}(\tau) d\tau$, Eq. (17) becomes:

$$576 \quad \langle \Delta \tilde{\mathbf{r}}_\alpha^2|_{x,y,z} \rangle = \langle \mathbf{u}|_{x,y,z}^2 \rangle \Delta t^2 \quad (18)$$

577 In the central part of the deep-fryer where the flow rate was the highest, correlation time $\Lambda|_{0,0,0}$

578 was about 24 ± 8 s. As a result, choosing $\Delta t \approx 0.1$ s $\ll \Lambda|_{0,0,0}$ justified that the contribution of

579 velocity fluctuations could be described as random ballistic trajectories (*i.e.*, proportional to

580 time). The decomposition of hydroperoxides was simulated using a root mean square

581 $\langle \mathbf{u}|_{x,y,z}^2 \rangle^{1/2} = 0.025 \mathbf{U}|_{x,y,z}$ (*i.e.*, 95% of fluctuations $\pm 5\%$), enabling smooth trajectories of

582 particles as experimentally observed in Figure 9b, while enabling particles to explore the entire

583 bath.

584 As a scalar field, temperature fluctuations are passively affected by the turbulent velocity field.

585 They decorrelated, therefore, almost similarly as velocity on time scales, Δt (see Figure 9b),

586 where L is the largest eddy scale, typically half-width. On time scales commensurable to Δt ,

587 several complications complicated the sampling of thermal fluctuations as reported in Refs.

588 [74-77] In liquids with high Prandtl numbers as oil, intense sources and intermittently rising

589 plumes were responsible for strong memory effects, including the persistence of temperature

590 fronts and profiles mimicking the shape of heating elements (see Figures 5 and 9). In the sake

591 of simplicity, turbulent variations of temperatures were introduced in our Lagrangian

592 formulation by authorizing the visited temperature $T|_{x,y,z}$ to fluctuate as a random white noise

593 normally distributed around 0 with a standard deviation proportional to $\frac{T|_{x,y,z} - 70}{T_{skin} - 70} 5^\circ\text{C}$. The

proposed noise scaling reproduced minimal fluctuations within the stagnant region and maximal in heated ones as experimentally assessed.

Though hydroperoxides may be present at the beginning of the heating cycle in the oil bath, they are continuously regenerated at the extreme surface. As a result, the trajectories of fluid particles emitted from the surface are more relevant to envision their fate in the oil bath. Typical fluid particle trajectories originating from the surface, in the median plane ($Z = 0$), and below the heating element are shown in Figure 10. They correspond to a convective transport longer than 1200 s. The rapid recirculation from the heating element back to the free surface confirms that an oil particle transporting hydroperoxides may be rapidly exposed again to atmospheric oxygen, facilitating their renewal. The recirculation above the heating element much faster than the decomposition rate of hydroperoxides (between $5 \cdot 10^{-4}$ and $1 \cdot 10^{-3} \text{ s}^{-1}$ at 160°C) justifies that they are decomposed at a steady rate at frying temperature.

In detail, recirculation loops were similar whether the particles came from the surface (Figure 10a-d) or the bulk oil above the heating element (Figure 10e-h). Particles close to the vertical symmetry plane $Y = 0$ remained almost confined within the plane XY . Outside the central region, particles were oriented along the main cross-sections (diagonal planes), exploring all corners. The merging of ascending plumes into one single central chimney forced the convergence of trajectories towards the symmetry axis $X = Y = 0$. The outside branches followed the shape of the oil bath and the symmetry planes while avoiding the inner part of the loops. This configuration maximizes the exposure to high temperature (path along the heating resistor) and oxygen (path along the free surface). Mixing times were evaluated using the concept of random walks in Figure 10m and defined as the average mixing time (τ) required to get a mean-square displacement (MSD) equal to the surface area of the explorable section. Mixing was said isotropic when MSD grew similarly along the main axes of the cross-section.

618 By analogy with diffusion on a line of length L , the mixing length along direction d is given
619 by $6 \max(MSD_{along\ d})$. Along direction X and Z, MSD increased proportionally with vising
620 time (parabolic with $\sqrt{\tau}$) in a very similar manner in less than 200 s. This behavior was typical
621 of uncorrelated displacements and corresponded to a maximum visited distance of 67 ± 3 mm,
622 which was periodically achieved approximately every 460 ± 20 s. Along Y, displacements
623 followed ballistic trajectories proportional to τ . Forty-minutes were required to visit half-
624 length of the deep-fryer without reaching a perfect mixing, while it was obtained in almost 3
625 minutes along the half-section of XZ.

626 The incursions under the heating element from the upper part of the bath remained exceptional
627 and brief (see Figure 10c). The particles under the heating element move essentially
628 horizontally at a very low speed due to pressure fluctuations. The difference in viscosity on
629 both sides prevents mixing. The zone is stagnant (Figure 10i-l) and does not exhibit any
630 significant turnover under simulated conditions (first ten minutes of heating). These conditions
631 are responsible for the long duration (two hours) needed to reach a steady thermal regime under
632 the heating resistor. Lower temperatures during the first ten minutes exacerbated dead volume
633 effects.

Figure 10: Simulated trajectories originated from (a-d) the surface (5 trajectories), (e-h) the median plane ($Z=0$, 5 trajectories) and (i-l) the bottom of the deep-fryer (40 trajectories): XZ (b,f,j), YZ (c,g,k) and XY (d,h,l) views. For each trajectory, starting and final points are plotted with triangle and square symbols, respectively. The plane of the heating element is materialized in red. (m) mean-square displacement (MSD) versus the square root of mixing time τ .

640 The vertical distributions of particles on short and long-time scales are plotted in Figure 11,
641 based on the sampling of more than 3×10^3 trajectories starting from the top, median, and bottom
642 positions. On short time scales, the vertical dispersion was faster from the median position than
643 from top and bottom ones. Residence times were indeed much longer at the free surface and
644 bottom (see Figure 10). On longer time scales, dispersions were similar from top and median
645 positions almost uniform, but with large fluctuations in time. Vertical mixing times were above
646 ca. 10^2 s and beyond 10^4 s above and below the heating element, respectively. As a result, only
647 $2 \pm 1\%$ of particles initially present in the cold zone could reach the region above (Figure 11f).
648 The risk of accumulation of hydroperoxides in the cold zone by convection was low during
649 initial heating and temperature holding. On the corollary, hydroperoxides present at the
650 beginning of heating would decompose very slowly in the stagnant region without escaping.
651 Without mixing and in extreme anoxia, polymerization and cyclization termination reactions
652 (exothermic) will dominate, whereas scission reactions (endothermic) would dominate
653 immediately above the heating element due to much higher temperatures and rapid renewal.
654 The production of volatile compounds far from the surface, where they are finally desorbed,
655 has been previously characterized by local sampling [10].

Figure 11: position distributions of oil particles with time according to the starting point from the surface (a-b), the median plan (c,d) and under the heating element (e,f). The red dotted lines represent the initial position of the particles along Z.

The decomposition of hydroperoxides in anoxia was simulated during four hours, starting from a uniform initial distribution in the deep-fryer, mimicking a real production cycle using sunflower oil. The effective decomposition for the regions above and below the heating element are compared with experimental values in Figure 12. The initial hydroperoxides were generated by bubbling air at 140°C (this temperature was shown to maximize hydroperoxide production in a reasonable time according to Ref. [11]). The initial composition in hydroperoxides was reconstructed from Ref. [11]. Experimentally, only the total amount of hydroperoxides was measured by FTIR [10]. The concentration in hydroperoxides was integrated along $1.2 \cdot 10^3$ trajectories initiated from equispaced points distributed uniformly via Eq.(11) and calculated independently with Eq.(12) from the distribution of residence times in temperature in the bath

671 as shown in Figure 12a. The separation between upper and lower regions was artificially
672 imposed by the starting position, but the exchange between regions was permitted.

673 For the upper volume, single-particle tracking (denoted PT) and residence time (denoted RT)
674 approaches are theoretically equivalent for durations longer than mixing time (~3 min along
675 XY). In this case, the exploration of regions at different temperatures is independent of the
676 order in which they are visited. Residence times depicted in Figure 12a were sampled from
677 random walks initiated from the upper region to avoid sampling biases due to hydroperoxides
678 decomposing faster than the time of passages from one region to the next (see justification in
679 the general discussion of Ref. [78]). The distribution for particles originating from arbitrary
680 positions is shown in Figure 9c. Only the PT approach gives access to the variability within the
681 deep-fryer due to dead volumes or overheated regions close to the heating element. More than
682 60% of PT values were indiscernible from RT determinations. Only three values were
683 significantly above and corresponded trajectories reaching the bottom region underneath the
684 heating element. Lower values were comparatively more frequent and were observed as soon
685 as the trajectory approached the heating element (with temperatures above 160°C), leading to
686 much faster decomposition. The detailed reconstruction for each hydroperoxides showed that,
687 though hydroperoxides from oleic (L_1OOH) and linoleic fatty esters (L_2OOH) were produced
688 in almost similar amounts in the bubbling reactor, the second decompose four times faster.
689 L_2OOH were all depleted in one hour whereas only half of L_1OOH was. During a typical
690 production cycle of one hour (heating, temperature holding, frying, cooling), these results
691 would demonstrate that L_2OOH would responsible for most of the inconvenience (smell,
692 fouling, loss of nutritional value) whereas L_1OOH would certainly reinitiate the oxidation of
693 lipids during the next production cycle.

694 For the lower region, thermal equilibration times (~ 2 hours) much longer than simulated heating
695 times (10 min) make simulated temperatures ($\sim 70^\circ\text{C}$) unsuitable for predicting the
696 decomposition of hydroperoxides. A constant temperature of 135°C close to experimental
697 measurements ($135 \pm 3^\circ\text{C}$) was applied instead. Since the region was uniform in temperature, no
698 PT results are shown. It is nevertheless underlined that the displacements are slow in the
699 stagnant region (see Figure 10l). Since the exchange between upper and lower regions was
700 minimal, the proposed approximation led to excellent predictions below the resistance during
701 the two first hours. Beyond two hours, their amount was overestimated due to a significant mass
702 transfer loss by diffusion and advection.

Figure 12: Residence time at each temperature calculated for 1200 trajectories (a) and comparison between measured and predicted values of LOOH concentration in the top and bottom regions (b)

E. *Effect of deep-fryer design*

Since the lifetime of hydroperoxides is longer than vertical mixing times, the distribution of residence times and temperatures govern the kinetics of decomposition of hydroperoxides. Figure 13 shows the oil flow structure and residence times within a deep-fryer directly heating from a rounded bottom and a limited cold zone. Heating elements are located at the top-end and at the bottom of the rounded part of the tank. Depicted simulations showed similar temperatures averaged over the entire oil volume but with different distributions (Figure 13b). The theoretical effects of the decomposition of hydroperoxides is shown in Figure 13c. In the depicted configuration, the new design without cold zone doubled the effective lifetime of hydroperoxides. The effects could not be guessed without simulation as some effects are antagonist. The modified configuration introduced hot spots, but also accelerated the dispersion in a larger accessible volume. The higher efficiency originates from the rounded bottom performing the recirculation and the creation of three independent plumes.

Figure 13. (a) Anisothermal oil flow within a 4 L deep-fryer without cold zone and equipped with four heating coils (two at the bottom and two at the transition between the rounded bottom and the vertical walls). (b) Comparison of temperature residence times with the reference design (see Figure 9) at steady-state and (c) corresponding hydroperoxides decomposition.

V. Conclusions

Autoxidation of triacylglycerols during frying has previously been studied as a chemical problem without considering temperature spatial heterogeneities and the coupling with vertical recirculation of oil between the heating element and the free surface. The flow is structured

during the first minutes of heating with fluctuations that dissipate exponentially with the decrease of temperature difference between the hottest and coldest regions. The heating of the oil under the electrical element coils is, conversely, delayed by almost two hours. The stationary temperature is 30-40°C below the frying temperature set above the heating element. Temperature fluctuations ($\pm 3^\circ\text{C}$) in the frying region are much lower than spatial heterogeneities 70-80°C with strong variations of residence times of fluid parcels. At steady state, CFD simulations showed rapidly rising plumes rapidly reorienting along the free surface where they cooled before beginning their slow subduction. This process disperses triacylglycerols and their hydroperoxides in almost of one quarter of the deep-fryer. The merging of several plumes in the central region generates a strong updraft forcing periodic exposure of hydroperoxides to high temperatures with pseudo-periods ranging from 3 to 5 minutes. The orientation of streamlines parallel to the free surface favors the dissolution of oxygen and thus the formation of hydroperoxides. The lifetime of hydroperoxides depends strongly on parent fatty esters at low and intermediate temperatures but in a less extent at frying temperatures. The presence of cold regions is essential to the preservation of unsaturated fatty esters, with the highest nutritional value. By contrast, hot surfaces destroy without differentiation all fatty esters. Transfer across the symmetry planes and mass transfer between the cold and the frying regions remains infrequent.

Since the time scales of hydroperoxide decomposition and vertical mixing times are separable, the decomposition kinetics of hydroperoxides and the rate of oxidation can be reconstructed from the distribution of residence times at different temperatures. This simplifying assumption facilitates the exploration of the relationship between fryer design and oil life by CFD simulations. The principles of a concurrent design methodology were outlined for two immersion fryers with a single heating plane in a parallelepipedic tank (standard design) and in a tank with a rounded bottom and two heating planes. Increasing the oil height and reducing the

cross-sectional area reduces the exposure to oxygen and extends the useful volume for frying. Larger volumes reduce the need for extreme temperatures. Current analyses do not take into account the presence of the basket and the product which can not only modify the structure of the flow and the product. Preliminary studies (results not shown) have shown that elements that obstruct the vertical flow are responsible for vertical temperature stratification and hot spots. This study demonstrates the strong spatialization of oxidation radical reactions. The upward velocities although fast in the central part of the fryer are insufficient to justify a transport of highly unstable alkoxy, hydroperoxy and alkyl radicals (lifetimes of the order of microseconds) from the heating elements to the free surface. The decomposition of hydroperoxides in depth and in anoxia produces essentially scission compounds in competition with the polymerization reactions responsible for the fouling of the heating surfaces. The coupling between the production of volatile organic compounds by scission, their transport and their desorption at the surface will be detailed in a companion paper.

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Declaration of interest

The authors declare no conflict of interest.

778

779 **Data availability statement**

780 The data that support the findings of this study are available from the corresponding author
781 upon reasonable request.

782

783 **Appendix A: Simplified oxidation model in mixture**

784 As the propagation via alkoxy and hydroxyl radicals and oxygen addition are several
785 magnitudes faster than the hydrogen abstraction via peroxy radicals and hydroperoxide
786 decomposition [19], the lumped mass balance reads:

$$\begin{aligned} \frac{d[L_iOOH]}{dt} &= -k_{d_i}(T)[L_iOOH] + k_{p_i}(T, [O_2])[L_iH] \\ \frac{d[L_iH]}{dt} &= -k_{p_i}(T, [O_2])[L_iH] \end{aligned} \quad (19)$$

788 where $\{k_{d_i}\}_{i=1,2,3}(T)$ and $\{k_{p_i}\}_{i=1,2,3}(T, [O_2])$ are the temperature dependent reaction rates of
789 decomposition and apparent propagation, respectively. By definition, the apparent reaction rate
790 $k_{p_i} = 0$ when $[O_2] = 0$.

791 Simplified model (Eq. (7)) is applicable to any isothermal dataset in anoxia and in oxygenated
792 conditions if k_{p_i} constants are determined independently. Following Refs. [79, 80], the equality
793 $k_{p_3} = 2k_{p_2}$ holds.

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