For submission to *Foods*

Title: Comparative 1H NMR-Based Chemometric Evaluations of the Time-Dependent Generation of Aldehydic Lipid Oxidation Products in Culinary Oils Exposed to Laboratory-Simulated Shallow Frying Episodes: Differential Patterns Observed for Omega-3 Fatty Acid-Containing Soybean Oils

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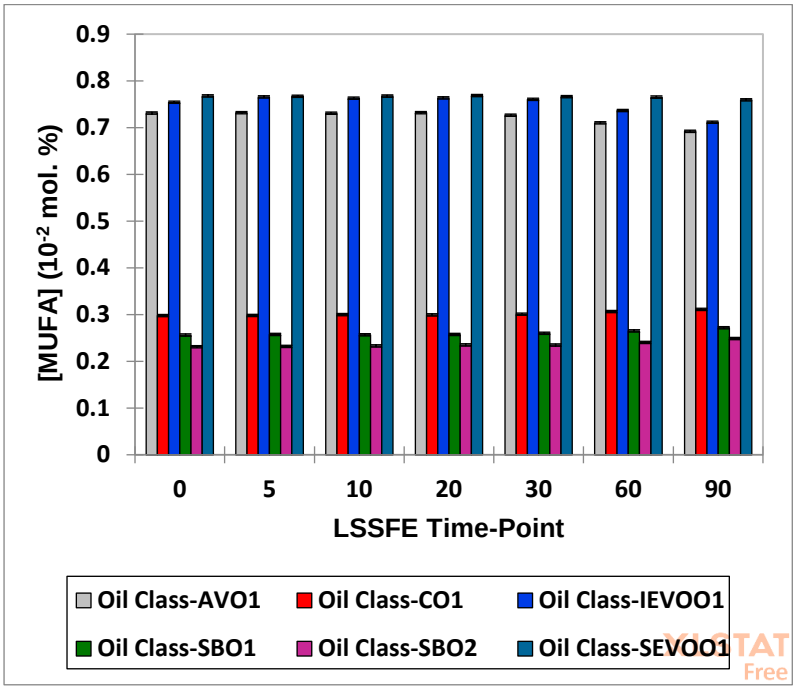
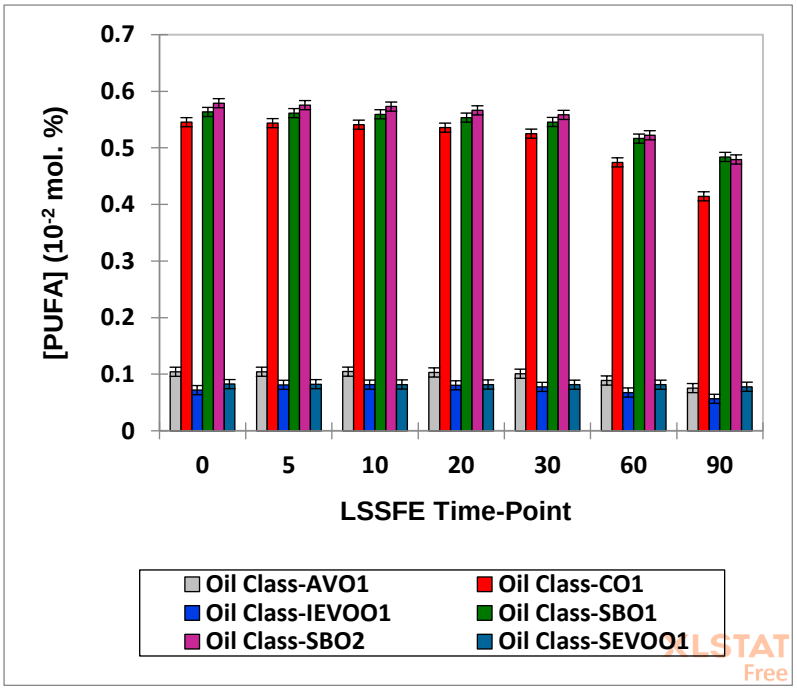
SUPPLEMENTARY MATERIALS SECTION

Figure S1

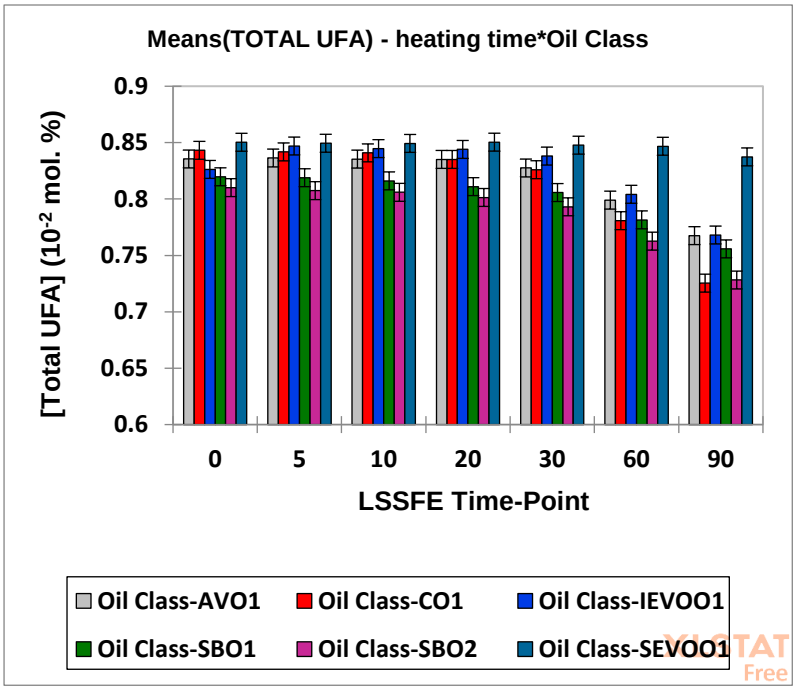
(a)


0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
[MUFA] (10-2 mol. %)
0
5
10
20
30
60
90
LSSFE Time-Point
Oil Class-AVO1
Oil Class-CO1
Oil Class-IEVOO1
Oil Class-SBO1
Oil Class-SBO2
Oil Class-SEVOO1
XLSTAT
Free

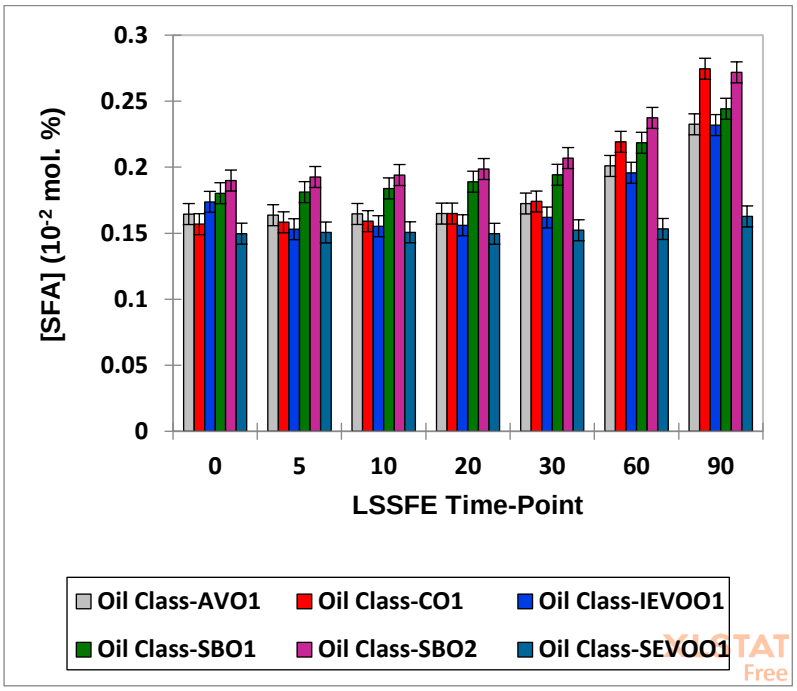
(b)


0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
[PUFA] (10-2 mol. %)
0
5
10
20
30
60
90
LSSFE Time-Point
Oil Class-AVO1
Oil Class-CO1
Oil Class-IEVOO1
Oil Class-SBO1
Oil Class-SBO2
Oil Class-SEVOO1
XLSTAT
Free

(c)


Means(TOTAL UFA) - heating time*Oil Class
[Total UFA] (10-2 mol. %)
0.9
0.85
0.8
0.75
0.7
0.65
0.6
0
5
10
20
30
60
90
LSSFE Time-Point
Oil Class-AVO1
Oil Class-CO1
Oil Class-IEVOO1
Oil Class-SBO1
Oil Class-SBO2
Oil Class-SEVOO1
XLSTAT
Free

(d)


[SFA] (10-2 mol. %)
0.3
0.25
0.2
0.15
0.1
0.05
0
0
5
10
20
30
60
90
LSSFE Time-Point
Oil Class-AVO1
Oil Class-CO1
Oil Class-IEVOO1
Oil Class-SBO1
Oil Class-SBO2
Oil Class-SEVOO1
XLSTAT
Free

(e)

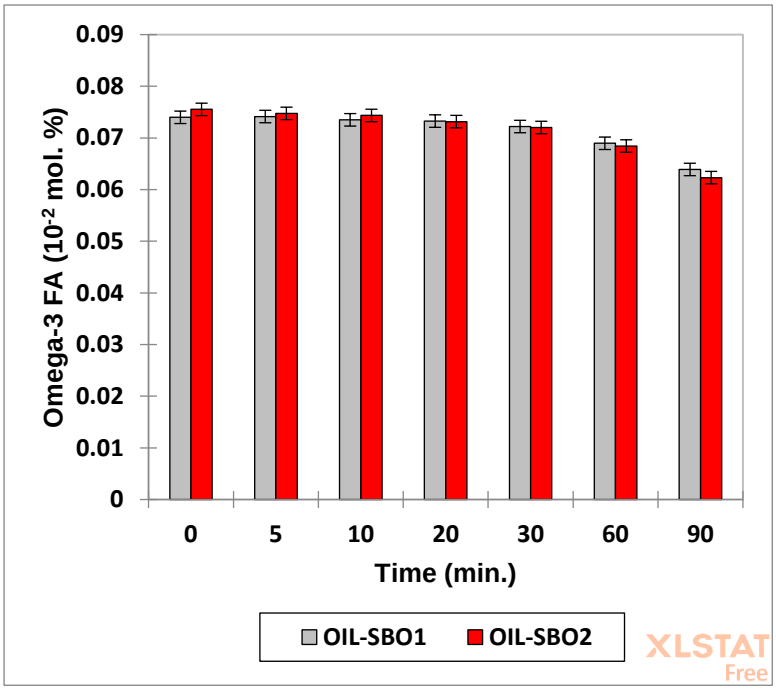


Figure S1. Bar diagram plot of mean±95% confidence intervals (CIs) for culinary oil contents of (a) MUFAs, (b) PUFAs, (c) Total UFAs and (d) SFAs in six culinary oils exposed to LSSFEs for periods of 0-90 min. **(**95% CIs in (b) are not clearly visible in S1(a) in view of their extremely small values). (e), Corresponding diagram for the omega-3 FA contents of the two soybean oils investigated. Abbreviations: SBO1 and SBO2, soybean oils 1 and 2; CO1, corn oil 1; AVO1, avocado oil 1; IEVOO1 and SEVOO1, Italian and Spanish extra-virgin olive oils 1 respectively.

Table S1. Relative MUFA, PUFA, ω-3, total unsaturated and saturated fatty acid contents (molar %) of culinary oils estimated by ^{1}H NMR analysis at LSSFE time-points of 0, 5, 10, 20, 30, 60 and 90 min. Oil type abbreviations: as Figure S1. *(w/w) contents provided by literature sources; na, not applicable.

Oil	Heating Time (min.)	Total MUFA Content (molar %)	Total PUFA Content (molar %)	Total UFA Content (molar %)	Total SFA Content (molar %)	ω-3 FA Content (molar %)
SEVOO1	0	76.78	8.25	85.03	14.97	0.80*
	5	76.70	8.24	84.94	15.06	na
	10	76.74	8.19	84.93	15.07	na
	20	76.86	8.18	85.04	14.96	na
	30	76.63	8.15	84.78	15.22	na
	60	76.53	8.15	84.68	15.32	na
	90	75.94	7.79	83.73	16.27	na
IEVOO1	0	75.43	7.19	82.63	17.37	0.80*
	5	76.57	8.12	84.70	15.30	na
	10	76.30	8.17	84.47	15.53	na
	20	76.36	8.03	84.40	15.60	na
	30	76.05	7.76	83.81	16.19	na
	60	75.36	7.52	82.88	17.12	na
	90	73.66	6.76	80.42	19.58	na
SBO1	0	25.62	56.35	81.97	18.03	7.40
	5	25.75	56.14	81.89	18.11	7.41
	10	25.67	55.93	81.61	18.39	7.35
	20	25.75	55.35	81.10	18.90	7.33
	30	26.00	54.58	80.57	19.43	7.22
	60	26.51	51.64	78.15	21.85	6.90
	90	27.18	48.40	75.57	24.43	6.39
SBO2	0	23.12	57.89	81.01	18.99	7.55
	5	23.19	57.55	80.74	19.26	7.48
	10	23.30	57.30	80.59	19.41	7.44
	20	23.51	56.62	80.14	19.86	7.32
	30	23.48	55.82	79.31	20.69	7.20
	60	24.03	52.41	76.44	23.56	6.84
	90	24.87	47.95	72.82	27.18	6.23
AVO1	0	73.11	10.43	83.55	16.45	0.95*
	5	73.19	10.44	83.64	16.36	na
	10	73.09	10.45	83.54	16.46	na
	20	73.20	10.31	83.51	16.49	na
	30	72.66	10.09	82.75	17.25	na
	60	71.02	8.88	79.90	20.10	na
	90	69.21	7.55	76.75	23.25	na
CO1	0	29.60	54.72	84.32	15.68	1.16*
	5	29.85	54.32	84.17	15.83	na
	10	29.85	54.24	84.09	15.91	na
	20	29.90	53.61	83.51	16.49	na
	30	30.04	52.56	82.60	17.40	na
	60	30.63	47.45	78.08	21.92	na
	90	31.17	41.37	72.54	27.46	na

Table S2. Mean aldehydic LOP concentrations (mmol./mol. FA) in culinary oils exposed to LSSFEs at 180°C FOR 0-90 min. Oil type abbreviations: as Figure S1.

Oil	Heating Time (min.)	Concentration (mmol./mol. FA)								
		(*E*)-2-Alkenals	(*E,E*)-2-4-Alkadienals	4,5-Epoxy-(*Z*)-2-alkenals	4-Hydroxy-/4-Hydroperoxy-(*E*)-2-alkenals	(*E,Z*)-2,4-Alkadienals	*n*-Alkanals	4-Oxo-*n*-alkanals	LMM *n*-Alkanals	(*Z*)-(2)-Alkenals
IEVOO1	**0**	0.026	0.060	0.001	0.004	0.004	0.045	0.000	0.000	0.000
	5	0.027	0.049	0.002	0.005	0.008	0.030	0.000	0.000	0.000
	10	0.048	0.043	0.006	0.013	0.016	0.053	0.000	0.000	0.000
	20	0.092	0.056	0.012	0.021	0.018	0.116	0.000	0.000	0.000
	30	0.256	0.112	0.033	0.023	0.029	0.255	0.000	0.000	0.000
	60	0.628	0.215	0.086	0.074	0.056	0.357	0.019	0.017	0.050
	90	1.540	0.478	0.212	0.178	0.121	0.700	0.029	0.026	0.088
SEVOO1	**0**	0.036	0.038	0.001	0.008	0.004	0.024	0.000	0.000	0.000
	5	0.025	0.041	0.000	0.014	0.008	0.025	0.000	0.000	0.000
	10	0.033	0.046	0.000	0.008	0.005	0.030	0.000	0.000	0.000
	20	0.070	0.029	0.004	0.011	0.013	0.038	0.000	0.000	0.000
	30	0.032	0.040	0.001	0.004	0.010	0.031	0.000	0.000	0.000
	60	0.041	0.033	0.003	0.011	0.013	0.049	0.000	0.000	0.000
	90	0.293	0.127	0.059	0.049	0.050	0.291	0.000	0.000	0.000
SBO1	**0**	0.051	0.045	0.012	0.014	0.021	0.094	0.000	0.000	0.000
	5	0.072	0.060	0.026	0.033	0.041	0.113	0.000	0.000	0.000
	10	0.129	0.127	0.045	0.058	0.062	0.157	0.000	0.000	0.000
	20	0.270	0.339	0.071	0.088	0.111	0.271	0.000	0.000	0.000
	30	0.556	0.709	0.159	0.170	0.205	0.493	0.000	0.000	0.000
	60	1.530	1.690	0.416	0.390	0.476	1.070	0.088	0.047	0.057
	90	2.660	2.450	0.616	0.589	0.529	1.400	0.142	0.053	0.092
SBO2	**0**	0.054	0.057	0.020	0.036	0.032	0.051	0.000	0.000	0.000
	5	0.089	0.106	0.037	0.039	0.049	0.091	0.000	0.000	0.000
	10	0.151	0.215	0.060	0.056	0.099	0.150	0.000	0.000	0.000
	20	0.402	0.564	0.127	0.120	0.218	0.342	0.000	0.000	0.000
	30	0.679	0.909	0.204	0.166	0.318	0.569	0.000	0.000	0.000
	60	1.930	2.190	0.517	0.395	0.672	1.300	0.106	0.050	0.084
	90	3.580	3.350	0.894	0.666	0.971	2.050	0.216	0.108	0.132
AVO1	**0**	0.047	0.025	0.015	0.020	0.013	0.062	0.000	0.000	0.000
	5	0.041	0.024	0.009	0.016	0.009	0.074	0.000	0.000	0.000
	10	0.072	0.037	0.018	0.018	0.012	0.099	0.000	0.000	0.000
	20	0.181	0.101	0.043	0.043	0.036	0.232	0.000	0.000	0.000
	30	0.470	0.238	0.078	0.062	0.060	0.437	0.020	0.017	0.018
	60	1.640	0.589	0.240	0.191	0.136	0.881	0.064	0.021	0.029
	90	3.210	0.795	0.367	0.311	0.146	1.260	0.102	0.028	0.058
CO1	**0**	0.80	0.126	0.042	0.032	0.057	0.143	0.000	0.000	0.000
	5	0.063	0.111	0.037	0.031	0.047	0.149	0.000	0.000	0.000

	10	0.091	0.117	0.039	0.030	0.050	0.167	0.000	0.000	0.000
	20	0.231	0.265	0.073	0.057	0.09	0.310	0.000	0.000	0.000
	30	0.555	0.599	0.156	0.130	0.206	0.564	0.000	0.000	0.000
	60	2.310	2.030	0.514	0.393	0.580	1.370	0.136	0.041	0.123
	90	4.500	3.050	0.887	0.676	0.780	2.120	0.211	0.058	0.209

Table S3. Total levels of unsaturated and saturated aldehydes (mmol./mol. FA) in each culinary oil exposed to LSSFEs for periods of 0, 5, 10, 20, 30, 60 and 90 min. Oil class abbreviations: as Figure S1.

Aldehyde Class	Oil Type	Time (min.)						
		0	5	10	20	30	60	90
		Aldehyde Concentration (mmol./mol. FA)						
Unsaturated	IEVOO1	0.09	0.09	0.13	0.20	0.45	1.10	2.62
	SEVOO1	0.09	0.09	0.09	0.13	0.09	0.10	0.58
	AO1	0.15	0.15	0.19	0.34	0.95	3.12	4.76
	SBO1	0.14	0.23	0.42	0.88	1.80	4.56	6.95
	SBO2	0.20	0.30	0.58	1.43	2.28	5.82	9.67
	CO1	0.34	0.29	0.33	0.72	1.65	5.95	10.10
Saturated	IEVOO1	0.04	0.03	0.05	0.12	0.26	0.42	0.75
	SEVOO1	0.02	0.03	0.03	0.04	0.03	0.05	0.29
	AO1	0.19	0.20	0.23	0.32	0.55	1.22	1.48
	SBO1	0.09	0.11	0.16	0.27	0.49	1.21	1.60
	SBO2	0.05	0.09	0.15	0.34	0.57	1.62	2.37
	CO1	0.14	0.15	0.17	0.31	0.56	1.54	2.39

Table S4. Least square mean (LSM) values for aldehydic LOP concentrations generated in soybean, corn, avocado and extra-virgin olive oils when exposed to LSSFE cycles for 0-90 min., and summary of all pairwise comparisons made to determine the significance of their differences between different culinary oil products (Bonferroni-corrected). (a), (*E*)-2-alkenals; (b), (*E,E*)-2-4-alkadienals; (c), 4,5-Epoxy-(*E*)-2-alkenals; (d), 4-OH-/4-OOH-(*E*)-2-alkenals; (e), (*E,Z*)-2,4-alkadienals; (f), *n*-alkanals; (g), 4-oxo-*n*-alkanals; (h) (*Z*)-2-alkenals; (i), low-molecular-mass (LMM) *n*-alkanals. For each aldehyde, culinary oil LSMs which are significantly different from each other have differing letter codes (A-E). The statistical significance of differences between individual culinary oil products were determined by *post-hoc* ANOVA tests performed by the Bonferroni method. Oil product abbreviations correspond to those in Figure S1.

(a)						
Culinary Oil	**LSMs ((*E*)-2-Alkenals)**	**Significantly Different Groups**				
SEVOO	0.08	A				
IEVOO	0.71		B			
SBO1	0.75		B	C		
AVO1	0.81		B	C		
SBO2	0.98			C	D	
CO1	1.12				D	
(b)						
Culinary Oil	**LSMs ((*E,E*)-2-4-Alkadienals)**	**Groups**				
SEVOO1	0.05	A				
IEVOO1	0.20		B			
AVO1	0.26		B			
SBO1	0.77			C		
CO1	0.90			C		
SBO2	1.06				D	
(c)						
Culinary Oil	**LSMs (4,5-Epoxy-(*E*)-2-alkenals)**	**Groups**				
IEVVOO1	0.01	A				
SEVOO1	0.08		B			
AVO1	0.11		B			
SBO1	0.19			C		
CO1	0.25				D	
SBO2	0.27				D	
(d)						
Culinary Oil	**LSMs (4-OH-/4-OOH-(*E*)-2-Alkenals)**	**Groups**				
SEVOO1	0.02	A				
IEVOO1	0.08		B			
AVO1	0.09		B			

SBO1	0.19			C		
CO1	0.19			C		
SBO2	0.21			C		
(e)						
Culinary Oil	**LSMs ((*E,Z*)-2,4-Alkadienals)**	**Groups**				
SEVOO1	0.01	A				
IEVOO1	0.05	A	B			
AVO1	0.06		B			
SBO1	0.21			C		
CO1	0.26				D	
SBO2	0.34					E
(f)						
Culinary Oil	**LSMs (*n*-Alkanals)**	**Groups**				
SEVOO1	0.07	A				
IEVOO1	0.32		B			
AVO1	0.43			C		
SBO1	0.51			C		
SBO2	0.65				D	
CO1	0.69				D	
(g)						
Culinary Oil	**LSMs (4-Oxo-*n*-alkanals)**	**Groups**				
SEVOO1	0.00	A				
IEVOO1	0.01	A	B			
AVO1	0.01	A	B	C		
SBO1	0.03		B	C	D	
SBO2	0.05			C	D	
CO1	0.05				D	
(h)						
Culinary Oil	**LSMs ((*Z*)-2-Alkenals)**	**Groups**				
SEVOO1	0.00	A				
IEVOO1	0.02	A	B			
SBO1	0.02	A	B			
AVO1	0.03		B	C		
SBO2	0.03		B	C		
CO1	0.05			C		
(i)						
Culinary Oil	**LSMs (LMM *n*-Alkanals)**	**Groups**				
SEVOO1	0.00	A				
IEVOO1	0.01	A	B			

AVO1	0.01		B	C		
CO1	0.01		B	C	D	
SBO1	0.02			C	D	
SBO2	0.02				D	