Food Research 6 (4) : 128 - 137 (August 2022)
Journal homepage: https://www.myfoodresearch.com

FOOD RESEARCH

FULL PAPER

Identification of cyclic fatty acids in frying oil by NMR

*Shaker, M.A., Marwa, A.A, Aml, R.T. and Ahmed, A.E.

Oils and Fats Research Department, Food Technology Research Institute, Agricultural Research Centre, Giza, Egypt

Article history:
Received: 3 August 2021
Received in revised form: 17 September 2021
Accepted: 19 October 2021
Available Online: 14 July 2022

Keywords:
Cyclic fatty acids,
Frying process,
GC,
NMR,
Sunflower oil

DOI:
https://doi.org/10.26656/fr.2017.6(4).577

Abstract

The main aim of the present research was to identify and estimate cyclic fatty acids that form during the frying process by Nuclear Magnetic Resonance (NMR) in oils that were used in the frying of french fries and fresh potatoes by frequent replenishment or without it. The potato fingers (1×1×4 cm) were fried in sunflower oil (3L), using the three systems designed: 1) sunflower oil without replacement oil, 2) sunflower oil with replacement oil, and 3) the oil extracted from commercial french fries. In addition, some chemicals (% FFA, peroxide value, polymer %, polar % and oxidized fatty acids content) and some physical characteristics (refractive index, viscosity and colour) of fresh and fried oils were determined. Also, fatty acids profile by GC for sunflower oil and extracted oil from french fries were determined. The results indicated that all physical and chemical properties of fried oil used in this work increased when the frying time increased at 180±5˚C for 30 hrs, 5 hr/day. Cyclic fatty acids could be identified using the NMR. Finally, the results indicate the possibility of using a device to identify the presence of cyclic fatty acids in frying oils.

1. Introduction

Deep-fat frying is widely used in food preparation because it provides appealing characteristics. The fat or oil acts as a heat transfer medium and as an important ingredient of fried food. As a consequence, fried foods are considered a significant part of the diet. In addition, consumption of fried frozen pre-fried foods has greatly increased during the last decade (Varela *et al.,* 1996). During the frying process, various chemical reactions occur, such as oxidation, hydrolysis, polymerization, isomerization, and cyclization (Cuesta *et al.,* 1993; Romero *et al.,* 1998). Thus, the physicochemical characteristics of the oil are affected. This thermal degradation should be studied not only for technological reasons (production of fried foods with acceptable qualities) but also for safety and nutrition because it is now known that some polar compounds from frying fats can present certain toxicity (López *et al.,* 1995). In addition, numerous cyclic fatty acids are formed in vegetable oils at temperatures ≥200°C. Their structures, occurrence, and biological effects have been reviewed (Sébédio and Grand, 1989). These compounds are potentially toxic and have been detected at low, but varying, levels (0.01–0.7%) in commercial frying oil. The levels required to produce a physiological effect are unknown.

Vegetable oil has wonderful attention as a renewable resource in the background of environmental concerns and fossil fuel depletion (Meher *et al.*, 2006; Kouzu *et al.,* 2008; Desroches *et al.,* 2012; Atabani *et al*., 2013; Talebian-Kiakalaieh *et al.,* 2013). Dimer acids, produced by the dimerization of unsaturated fatty acids from fried vegetable oil, are high value-added products and are widely used as adhesives (Kadam *et al.,* 2014; Li *et al.,* 2014), plastic additives (Ko *et al.,* 2013; Li *et al.,* 2014) and lubricants (Lee *et al.,* 201).

Several synthesis methods have been investigated to date to obtain dimer acids. However, the reported methods inevitably produce a mixture of several isomers of dimer acids including acyclic and cyclic dimer acids (CDAs) owing to the use of different raw materials. Due to several possible couplings, synthesized CDAs may have several chemically different functional groups on the cyclic ring. Moreover, both the detection and separation of specific dimer acids from the product mixture are difficult due to in molecular weights of the acids. The development of analysis techniques for such complex compounds is required like nuclear magnetic resonance (NMR).

The present research aimed to identify and determine the cyclic fatty acids that form during the frying process

*Corresponding author.
Email: *dr_shakerarafat@yahoo.com*

eISSN: 2550-2166
Published by Rynnye Lyan Resources

by NMR in oils that were used in the frying of french fries and fresh potatoes by frequent replenishment or without it. In addition to all chemical and physicochemical characteristics that happened during the frying process were determined.

2. Materials and methods

2.1 Materials

Potatoes (Cara variety) were purchased from a local market, El-Qalubiya Governorate, Egypt. french fries were obtained from Farm Frites-Egypt (The International Company for Agricultural Development-10th of Ramadan City). Sunflower oil was purchased from a local market. Chemical and solvents of analytical grade were purchased from El-Gomhouriya Company for Trade Chemical and Drugs, Cairo Governorate, Egypt.

2.2 Methods

Local market potatoes were washed peeled and cut into fingers dimensions of 1×1×4 cm using a manual cutting machine.

2.2.1 Frying process

There were three different experiments, in each experiment 3 kg of sunflower oil was used in the deep-frying process, which was carried out using a domestic fryer (Model 7122 A, Tefal super 500 Delux, France) at 180±5°C. The first experiment was conducted using pre-fried potatoes. The second design used potatoes from a local market (french fries), but the oil was substituted every 5 hrs. In the third procedure, potatoes from a local market without substitution were used. The period of frying was 30 hrs (5 hrs daily for 6 consecutive days), in 100 mL of oil, withdrawn at the end of frying and the oil was left to cool to room temperature, it was then stored in dark bottles at -18°C till further analyses.

2.2.2 Determination of moisture and oil uptake

Moisture content and the oil uptake of sample potatoes were determined according to the method described by the AOAC (2016).

2.2.3 Determination of some physico-chemical properties

Refractive index (RI) at 40°C, free fatty acids (FFA) (as oleic acid) and peroxide value (PV) (meq O_2/kg oil) were determined according to the method described by the AOAC (2016). The colour of oil samples was measured using a Lovibond Tintometer Model F, 5.25-inch cell, according to AOAC (2016).

2.2.4 Viscosity

Viscosity (cP) was monitored using Brookfield Viscometer RVDV Spindle SC4-21 connected to water bath Brook-field TC500. Viscosity determination was carried out at 40±0.1°C according to the method described by Howard (1991).

2.2.5 Polymer content

Polymer content (PC) of oil samples was determined following the method mentioned by Wu and Nawar (1986).

2.2.6 Polar content

Total polar compounds (TPC) of the oil samples were determined using column chromatography according to the method described by (Waltking and Wessels, 1981).

2.2.7 Oxidized fatty acids content

Petroleum ether-insoluble oxidized fatty acids were determined according to the method described by (Billek *et al.,*1978).

2.2.8 Determination of the fatty acids profile

Fatty acids were carried out by preparation of methyl ester followed by the identification of methyl esters using an Agilent 6890 series Gas Chromatograph apparatus equipped with a DB23 (60 m × 0.32) (ISO, 2011).

2.2.9 NMR Spectral Analysis

The samples were dissolved in CDCl3 (750 µL) and an accurately measured volume of the solution (550 µL) was transferred to a 5 mm NMR tube. ^{1}H NMR spectra were recorded with a Varian 400 spectrometer advanced capillary tube system. Typically, 50 scans were collected into 32K data points over a spectral width of 0−16 ppm with a relaxation delay of 1 s and an acquisition time of 1.7 s. Prior to Fourier Transformation (FT), an exponential weighting factor corresponding to a line broadening of 0.3 Hz was applied. The spectra were phased corrected and integrated automatically. When necessary, accurate integration was performed manually for the peaks of interest.

3. Results and discussion

It is important in any scientific study to shed light on the raw materials that are used in the preparation of food. Table 1 indicates some properties of fresh sunflower oil, as well as the oil extracted from french fries, and the fatty acid composition in both samples. The results showed that the refractive index (at 40°C), viscosity (at

Table 1. Fatty acids composition of sunflower oil and extracted oil from french fries.

Characters and fatty acids	Oil extract from french fries (%)	Sunflower oil (%)
Refractive index (at 40°C)	1.4581	1.4730
Viscosity (CP) (at 40°C)	45.90	58.00
Red color (at yellow 35)	0.1	0.00
Acidity (%) as oleic acids	0.21	0.02
PV (meq. O_2/Kg oil)	0.75	0.50
Polymer content (%)	0.001	0.00
Polar content (%)	3.50	2.50
Oxidized fatty acids (%)	0.00	0.00
Fatty acids		
$C_{6:0}$	0.18	0.00
$C_{12:0}$	0.21	0.00
$C_{14:0}$	0.90	0.06
$C_{16:0}$	36.75	6.49
$C_{16:1}$	0.19	0.10
$C_{17:0}$	0.09	0.40
$C_{17:1}$	0.01	0.02
$C_{18:0}$	4.17	3.45
$C_{18:1}$	41.92	25.79
$C_{18:2T}$	0.13	0.64
$C_{18:2}$	14.02	62.1
$C_{18:3}$	0.64	0.19
$C_{20:0}$	0.39	0.26
$C_{20:1}$	0.23	0.17
$C_{22:0}$	0.17	0.69
Σ Total saturated fatty acids	42.86	11.35
Σ Total unsaturated fatty acids	57.14	88.65
Σ Total trans fatty acids	0.64	0.13
Σ Total cis fatty acids	99.36	99.87

40°C), red colour at (yellow 35), the free fatty acids (calculated as oleic acid %) and the peroxide value were 1.4581 and 1.4730, 45.90 and 58.00, 010 and 0.00, 0.21 and 0.02% and 0.75 and 0.50 for both samples, respectively. The results also show the values of polymer, polar contents and oxidizing fatty acids for both samples, which were 0.001 and 0.00%, 3.50 and 2.50% and 0.00 and 0.00%, respectively.

In addition, the fatty acids composition of both oil samples indicates that the predominant saturated fatty acid in the oil of both samples was palmitic acid (36.75 and 6.49%), followed by stearic acid (4.17 and 3.45%), the results also indicate a higher content of two acids in the oil extracted from french fries than fresh sunflower oil. In addition, oleic acid was found to be the predominant unsaturated fatty acid in both samples (41.92 and 25.79%), followed by linoleic acid (14.02 and 62.10%), respectively.

In the same context, the values of total saturated fatty acids for oil extracted from the french fries were higher (42.86%) than that of the sunflower oil (11.35%), and conversely, the values of the unsaturated fatty acid content in the sunflower oil were (88.65%) higher than the oil sample extracted from of french fries (57.14%). Also, the results in Table 1 indicate that the fresh sunflower oil sample contains a lower percentage of trans fatty acids (0.13%) than the oil sample extracted from french fries (0.64%). The differences in the characteristics oil sample and oil extracted from french fries may be due to the difference in both samples, which the results indicate that the first sample is sunflower oil and the second sample may be palm oil.

During the process of preparing fried foods in an oily medium, the moisture content of the food decreases with increasing time, and conversely, an increase in the oil content occurs in the fried food. Table 2 indicates that the moisture content of potato samples at the zero time of frying at 180±5˚C for 30 hrs was less than that of fresh potatoes. There has been a gradual decrease in the moisture content of all samples during the frying process may be due to the increased frying period, the rate of a decrease in moisture content of the french fries sample, and conversely, the rate of reduction in moisture content fresh sample fried in oil with replacement was similar to that of fresh sample fried in oil without substitution. The oil uptake percentage in the same table was 8% at zero time in french fries and this may be related to the previous treatment of the french fries one in the factory, it also had a clear higher percentage throughout the experiment than fresh potatoes. On the other hand, fried fresh potatoes using replenishment had the lowest percentage of oil uptake.

Table 2. Moisture content and oil uptake of frying french fries, fresh potatoes with frequent replenishment and fresh potatoes without replenishment.

Treatment	Frying time (hrs)	Moisture content (%)	Oil uptake (%)
French fries	0	68.93	8.00
	5	20.11	13.50
	10	21.20	15.60
	15	23.20	17.00
	20	22.90	17.90
	25	20.50	18.98
	30	19.60	20.01
Replenishment oil	0	79.59	0.00
	5	29.17	9.90
	10	30.56	10.50
	15	31.54	10.58
	20	30.50	10.94
	25	32.60	11.30
	30	32.90	11.90
Without replenishment Treatment	0	79.59	0.00
	5	30.65	9.90
	10	31.68	11.23
	15	33.70	11.90
	20	32.90	12.01
	25	33.10	13.02
	30	31.50	14.09

Table 3. Some physical characteristics of fresh and extracted oils from frying pre-fried frozen potatoes, fresh potatoes with frequent replenishment and fresh potatoes without replenishment during frying for 30 hrs.

Treatment	Frying time (hrs)	Refractive index (At 25°C)	Viscosity (cP) (at 25°C)	Red color (at yellow 35)
Fresh oil	0	1.4730	58.00	0.0
French fries	5	1.4739	61.00	1.6
	10	1.4745	64.50	2.3
	15	1.4758	70.00	3.86
	20	1.4775	75.00	6.4
	25	1.4781	79.00	8.4
	30	1.4793	85.00	10.3
Replenishment oil	5	1.4736	60.00	1.6
	10	1.4740	62.00	1.9
	15	1.4749	66.00	2.8
	20	1.4757	70.50	3.0
	25	1.4763	73.50	4.7
	30	1.4771	77.50	6.2
Without replenishment	5	1.4738	60.00	1.6
	10	1.4749	64.00	2.1
	15	1.4760	70.00	3.85
	20	1.4779	75.50	6.5
	25	1.4783	79.00	8.5
	30	1.4792	84.50	10.1

The results in Table 3 show the effect of the frying process on some physical characteristics (refractive index at 40°C, viscosity (cP) and colour as red units at 35 yellow units) of oils used in frying french fries and fresh potatoes using frequent replenishment or without it. The values of refractive index, viscosity and colour were 1.4730, 58.00 and 0.00 at zero time of the frying process at 180±5˚C, for 30 hrs 5 hrs /day, respectively. There was an increase in the refractive index values of french fries sample in sunflower oil from 1.4739 to 1.4793 and there was also an increase in the viscosity of the oil, where the value increased from 61.00 to 85.00 at the end of frying (30 hrs). In a related context, there was a clear change in the colour of the oil (medium) for frying the french fries sample, which the red colour value increased from 1.6 to 10.3 at the end of the frying period.

The results in Table 3 increment the refractive index values of the oil for frying fresh potatoes at 180±5˚C for 30 hrs, the increased value in refractive index from 1.4736 at 5 hrs from the beginning of frying to 1.4771 at the end of the frying period. Also, the viscosity of sunflower oil (medium of the frying) was increased gradually during the frying process, with the replacement oil. In this direction, the red colour value increased in the oil medium for frying fresh potatoes, with the replacement of part of the oil. Red colour values increased from 1.6 to 6.2 at the end of the frying period. Finally, the obtained results indicate that it is possible to rely on the properties of refractive index, viscosity and red colour as an indication of the state of deterioration in the oil as a frying medium in the experiment in which the oil was not replaced.

From the previous results, it is clear that the highest value is recorded in the oil sample as a frying medium for french fries. While the lowest value was in the sample of oil used as a medium for frying fresh potatoes with the replaced oil. Also, the data found that the high values of refractive index, viscosity and red colour in the oil sample as a medium for frying re-fried frozen potatoes may be due to the french fries, which contain an oil content of about 8%, this oil differs in its properties from the sunflower oil used as a medium for frying and was also exposed to heat previously, that may have affected its properties. Data in this table illustrated that refractive index, viscosity and colour increased due to increased frying time in the three experiments. These changes in the oil with frequent replacement were lower than in both oils used in french fries and fresh potatoes without replacement. These variations may be attributed to the dilution effect caused by the frequent replacement of fresh oil (Romero *et al.*, 2000).

The effect of the frying process on free fatty acids (FFA% as oleic acids), peroxide values (PV meq O_2/kg oil), polymer content (PC%) total polar compounds (TPC%) and oxidized fatty acids (OFA%) of oils used in frying process was studied and the results are tabulated in Table 4. It was found that FFA% increased by increasing the frying period in all the samples. This increment was higher in the oils used in frying fresh potatoes without replenishment and french fries compared to the oil used in fresh potatoes with replacements. When food is fried in heated oil, the moisture changes to steam, which evaporates with a bubbling action and gradually subsides as the food are fried. Water, steam, and oxygen initiate the chemical reactions in the frying of oil and food. Water, a weak nucleophile, attacks the ester linkage of triacylglycerols that produce di- and monoacylglycerols, glycerol, and free fatty acids. The other type of hydrolysis thermal hydrolysis takes place mainly within the oil phase rather than the water-oil interface. Free fatty acids are used to monitor the quality of frying oil (Chung *et al.,* 2004). Frequent replacement of frying oil with fresh oil slows down the hydrolysis of frying oil (Romero *et al.,*1998). Results in the Table 4 revealed that PV, which was used as a measurement of the primary products of oxidation, was sharply increased through the first 5 hrs in different experiments and continued rising but it was slow in the oil that was used in frying fresh potatoes that has been replaced. At the end of the experiment, the rising PV was not stable and began to decrease. This may be explained by the breakdown of the ester of triglycerides to produce carbonyl and aldehydic compounds as a result of secondary oxidation (Li *et al.,* 2014

Total polar compounds (TPC%) of oils indicate that the total amount of degradation compounds in frying oils was also determined and the results are tabulated in Table 4. Results showed that oil used in the frying process of french fries had affected the TPC% during the first 10 hrs when compared with other oils used in the frying process. However, in general, TPC% in the oil used in the frying of french fries and fresh potatoes without replenishment was the greatest if compared to oil that was used in the case of frying fresh potatoes with the frequent replenishment.

This trend of increment was also noticed when monitoring the changes in PC% for oils used in frying experiments, where sharp increments in PC% occurred during the first 10 hrs followed by a gradual increase at the end of the experiment. Also, these changes in PC% were high pronounced in oils used for frying french fries and fresh potatoes followed by the oil used in frying fresh potatoes with replenishment. Polymers are mainly responsible for the increase in viscosity, refractive index, specific gravity and contribute to the foaming tendency of heated oil (Wang *et al*., 2016). The formation of dimers and polymers depends on the oil type, frying temperature, and time of frying. As the amount of frying and its temperature increases, the amounts of polymers increase (Cuesta *et al.,* 1993; Takeoka *et al.,* 1997) as oxidized polymer compounds accelerate the oxidation of the oil. Polymers accelerate the degradation of the oil, increases the oil viscosity, reduces heat transfer, produces foam during deep-fat frying, and develop undesirable colours in the food. Moreover, the polymer compounds cause a high oil uptake in foods (Tseng *et al*., 1996). The results in the Table 4 revealed that values of the oxidized fatty acids increased with the increase in frying time in all treatments, but this increase was high in the oils that were used in the frying of french fries and fresh potatoes without replenishment.

Table 4. Chemical characteristics of fresh and extracted oils from frying pre-fried frozen potatoes, fresh potatoes with frequent replenishment and fresh potatoes without replenishment during the frying for 30 hrs.

Oils extracted from	Frying time (hr)	FFA (% as oleic acids)	PV (meq O_2/Kg oil)	Polymer contents (%)	Total Polar Compounds (%)	Oxidized fatty acid (%)
Fresh oil	0	0.02	0.50	0.00	2.50	0.00
French fries	5	0.35	3.80	0.185	6.34	0.39
	10	0.80	6.90	0.60	11.51	0.85
	15	0.96	10.60	1.01	16.54	1.29
	20	1.50	17.60	1.24	23.23	1.90
	25	2.10	24.75	2.99	27.02	3.10
	30	3.30	20.15	5.90	31.01	4.20
Replenishment oil	5	0.34	4.05	0.25	5.50	0.40
	10	0.45	4.90	0.43	8.50	0.70
	15	0.59	6.70	0.75	13.60	0.91
	20	0.90	8.60	0.95	19.01	1.05
	25	1.68	10.20	1.30	25.03	1.80
	30	2.41	13.80	1.95	28.50	2.01
Without replenishment oil	5	0.36	4.10	0.24	5.60	0.41
	10	0.89	7.10	0.59	10.90	0.79
	15	1.50	10.36	0.99	17.01	1.10
	20	2.13	18.34	1.25	25.10	1.70
	25	3.50	25.20	2.80	29.37	2.90
	30	4.66	23.20	5.50	32.40	4.50

3.1 Determination of cyclic fatty acids by NMR

NMR was used to determine the contents of different substances in complex mixtures, whereby quantitative ^{1}H NMR spectroscopy was also useful. NMR spectroscopy provides high selectivity and absolute quantification of specific compounds in a mixture using an internal standard (IS) reference material. The magnitude of the NMR peak is directly proportional to the number of nuclei and the molar concentration of the sample. Based on this intensity relationship, the concentration of the analyte can be measured by quantitative ^{1}H NMR using the ratio between the integral value of the sample's specific chemical shift and that of the IS (Ohtsuki *et al*., 2012; Ohtsuki *et al.,* 2013). The oxidation of edible oils and fats is a matter of major concern not only from the technological and economic point of view but also for safety reasons, due to the undesirable properties of some compounds produced in this process (Guillen and Ruiz 2001). In this experiment, NMR spectroscopy is a powerful technique able to investigate the thermodynamic properties of complex systems such as aldehydes, ketones, peroxides and hydrated proteins (Mallamace *et al*., 2015), cellulose (Corsaro *et al*., 2013), colloids (Mallamace *et al.,* 2015) Furthermore, the NMR technique usually considered the recognized analytical technique as well as Gas Chromatography and Mass Spectrometry (Gallo *et al.,* 2015). NMR experiments was performed by using a 500 MHz Joel.

Figure 1, Figure 2 and Figure 3 display the NMR results of added fresh oil, french fries and without added fresh oil, respectively in the frying process.

From the charts, two types of signals, first type find 9 signals at: 0.9 ppm for CH3 Methyl proton at the end of all acyl chains, (CH2). Methylene of acyl chains at 1.3 ppm, (CH2-CH2-CO) protons of acyl at 1.6 ppm, (CH2-CH=CH) Allylic methylene's at 2 ppm, CH2-CO protons of acyl moieties at 2.3 ppm, (=CH2-CH2-CH2=) Bis-allylic methylene's at 2.8 ppm, CH2-OCOR the methylene's (α) of glycerol unit at 4.1 ppm, CH2-OCOR. The methylene's (α') of glycerol unit at 4.3 ppm, CH-OCOR the methine (β) of glycerol unit at 5.3 ppm and CH=CH for the olefinic protons of all unsaturated fatty acids at 5.4 ppm. All these signals are found in all charts of sunflower oil NMR and it is considered a sunflower oil fingerprint.

From the results in Figure 1, in which 3 samples were analysed at different times: the first sample (5h) after 5 hrs of frying process: the second sample (15h) after 15 hrs of frying process and the third sample (25h) after 25 hrs of frying process; first sample (5h) added fresh oil throughout the frying process, in the second sample (15h) french fries without adding any fresh sunflower oil throughout frying process, in the third sample (25h) used fresh potatoes without adding any fresh sunflower oil throughout the frying process. Notice in Figure 1 the signal of the aldehydic group increased as follows, aldehydic signals in sample 3 (25h) were more than in sample 2 (15h) and more than in sample 1 (5 h), because the degradation of sunflower oil through different frying process increases, and produces more aldehydes as illustrated (Sacchi *et al.,* 1996; Owen *et al.* 2000; Esbensen *et al.*, 2002).

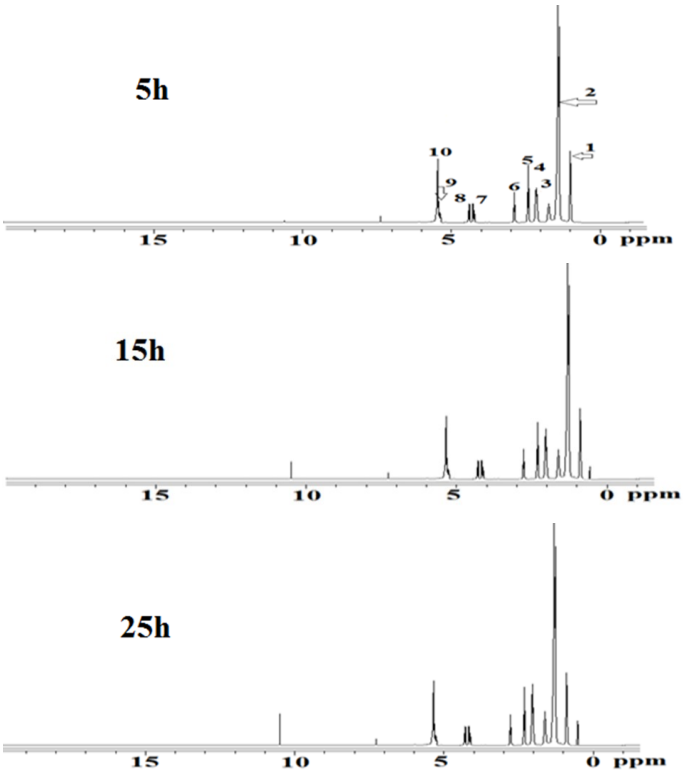

Figure 1. Assignment and description of the principal proton NMR signals with added fresh oil (5h, 15h and 25h).

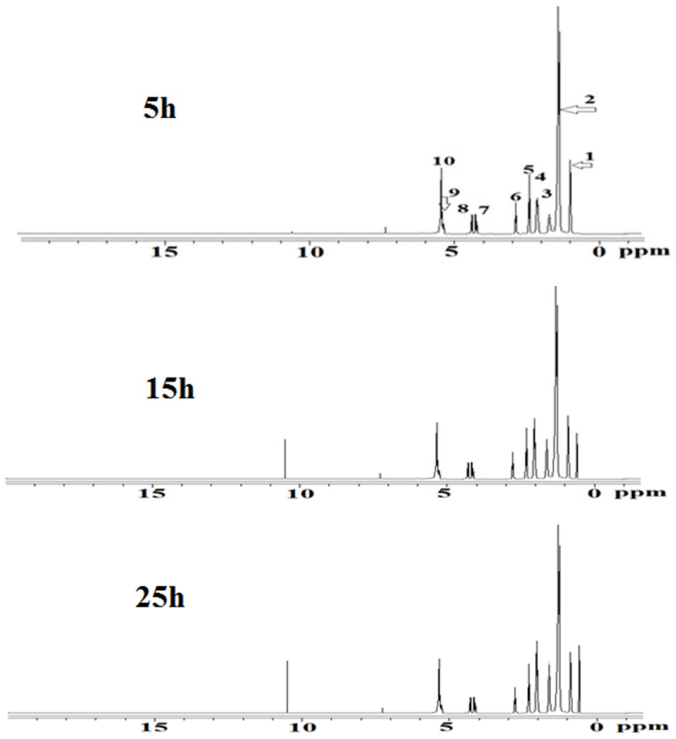

Figure 3. Assignment and description of the principal proton NMR signals without added fresh oil (5h, 15h and 25h).

The pattern in Figure 2 in sample 1 (5h), sample 2 (15h) and sample 3 (25 h) frying the sunflower oil for 5 hrs, 15 hrs and 30 hrs with french fries without adding any fresh sunflower oil throughout the frying process, notice the signal of aldehydic group increases as the aldehydic signals in sample 1 (5h) are less than in sample 2 (15h), and less than in sample 3 (25h), because the

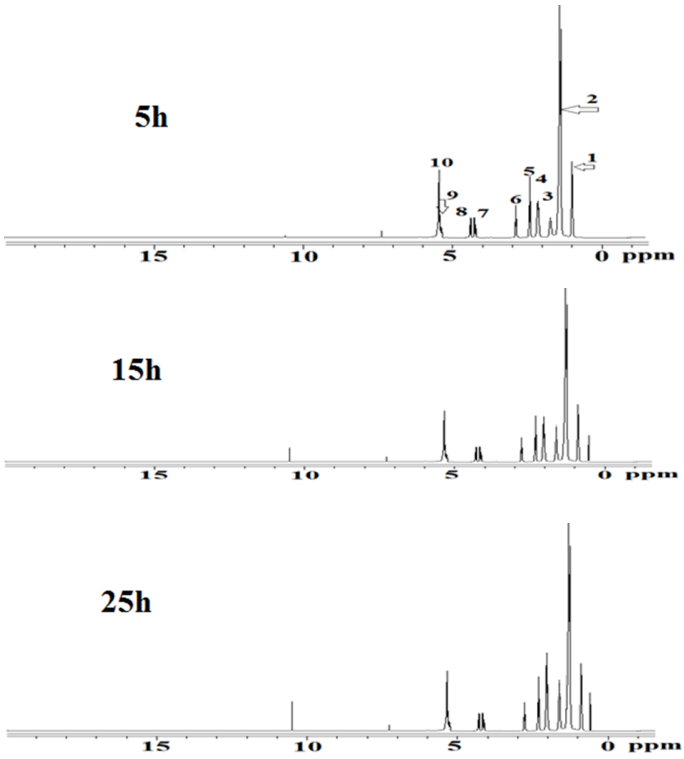

Figure 2. Assignment and description of the principal proton NMR signals with french fries (5h, 15h and 25h).

degradation of sunflower oil through different frying process increased, and produces more aldehydes as illustrated in the previous sample (a) (Sacchi *et al.,* 1996; Owen *et al.*, 2000; Esbensen *et al.*, 2002).

Finally, the pattern in Figure 3 in sample 1 (5h), sample 2 (15h) and sample 3 (25h) is shown when frying the sunflower oil for 5 hrs,15 hrs and 25 hrs using fresh potatoes without adding any fresh sunflower oil throughout the frying process, displays signals of an increased of aldehydic group where signals in sample 1 (5h) are less than in sample 2 (15h) and less than sample 3 (25h), because the degradation of sunflower oil through different frying process increases, and produce more aldehydes as illustrate in the previous discussion (Sacchi *et al.,* 1996; Owen *et al.*, 2000; Esbensen *et al.*, 2002).

From the above discussion, in the three experiments, it can be noticed that in the first sample (at 5 hrs) there was no appearance of an aldehydic group because the degradation did not start, in the second sample (15 hrs), notice the appearance of the aldehydic group due to the increase in degradation, finally at last sample at (25 hrs) the intensity of aldehydic increases drastically due to the increase of degradation by frying. Furthermore, by comparison, in the last sample (25h, 25h and 25h) in the three samples (Figures, 1, 2, and 3), it was noticeable that the intensity of the aldehydic group was more than in the non-added fresh oil frying process in the sample (3) than pre-fried frozen in the sample (2) and added fresh oil in sample (1).

eISSN: 2550-2166

In the same context, while frying the appearance of fatty acids containing a cyclopropene unit within the chain, the protons of the ring methylene were observed as a singlet at 0.73-0.75 ppm (Gosalbo *et al.,* 1993; Hartmann *et al.,* 1994). The signal at 1.57 ppm was caused by the protons of the methylene moieties β to the cyclopropene ring as well as those of C3 (Gosalbo *et al.,* 1993) or these signals were contained in the strong methylene peak (Hartmann *et al.,* 1994). The signal at 2.37 ppm was attributed to the four protons of the methylene moieties adjacent to the carbons carrying the cyclopropene ring (Gosalbo *et al.,* 1993) or a peak at 2.37 ppm caused by the protons at C2 and that α to the cyclopropene ring.

4. Conclusion

The cyclic fatty acids are formed during the frying process. It is possible by using the Nuclear Magnetic Resonance (NMR) apparatus was possible to identify the cyclic fatty acids in the frying oils. The results also concluded that the process of replacing a percentage of the oil used in the frying process increases the oil's survival in good condition. This was demonstrated by estimating some of the natural and chemical properties of fresh oil during different stages of the frying process.

References

AOAC. (2016). Official Methods of Analysis of AOAC International 20th ed. Gaithersburg, Maryland. USA: Association of Official Analytical Chemists,

Atabani, A.E., Silitonga, A.S., Ong, H.C., Mahlia, T.M.I., Masjuki, H.H., Badruddin, I.A. and Fayaz, H. (2013). Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions, biodiesel production, characteristics, engine performance and emissions production. *Renewable and Sustainable Energy Reviews*, 18, 211–245. https://doi.org/10.1016/j.rser.2012.10.013

Billek, G., Guhr, G. and Waibl, J. (1978). Quality assessment of used frying fats: a comparison of four methods. *Journal of the American Oil Chemical Society*, 55(10), 728-733. https://doi.org/10.1007/BF02665370

Chung, J., Lee, J. and Choe, E. (2004): Oxidative stability of soybean and sesame oil mixture during frying of flour dough. *Journal of Food Science*, 69 (7), 574–578. https://doi.org/10.1111/j.1365-2621.2004.tb13652.x

Corsaro, C., Mallamace, D., Łojewska, J., Mallamace, F., Pietronero, L. and Missori, M. (2013). Molecular degradation of ancient documents revealed by ^{1}H HR -MAS NMR spectroscopy, *Scientific Reports*, 3, 2896. https://doi.org/10.1038/srep02896

Cuesta, C., Sanchez-Muniz, F.J., Garrido-Polonio, C., Lopez-Varela, S. and Arroyo, R. (1993). Thermoxidative and hydrolytic changes in sunflower oil used in frying with a fast turnover of fresh oil. *Journal of the American Oil Chemists' Society*, 70 (11), 1069–1073. https://doi.org/10.1007/BF02632144

Desroches, M., Escouvois, M., Auvergne, R., Caillol, S. and Boutevin, B. (2012). From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products. *Polymer Reviews*, 52(1), 38-79. https://doi.org/10.1080/15583724.2011.640443

Esbensen, K.H., Guyot, D., Westad, F. and Houmøller, L.P. (2002). Multivariate data analysis in practice: an introduction to multivariate data analysis and experimental design. 5th ed. Oslo, Norway: Camo Process AS.

Gallo, V., Intini, N., Mastrorilli, P., Latronico, M., Scapicchio, P., Triggiani, M., Bevilacqua, V., Fanizzi, P., Acquotti, D., Airoldi, C., Arnesano, F., Assfalg, M., Benevelli, F., Bertelli, D., Cagliani, L.R., Casadei, L., Marincola, F.C., Colafemmina, G., Consonni, R., Cosentino, C., Davalli, S., De Pascali, S.A., D'Aiuto, V., Faccini, A., Gobetto, R., Lamanna, R., Liguori, F., Longobardi, F., Mallamace, D., Mazzei, P., Menegazzo, I., Milone, S., Mucci, A., Napoli, C., Pertinhez, T., Rizzuti, A., Rocchigiani, L., Schievano, E., Sciubba, F., Sobolev, A., Tenori, L. and Valerio, M. (2015). Performance assessment in fingerprinting and multi component quantitative NMR analyses. *Analytical Chemistry*, 87 (13), 6709–6717. https://doi.org/10.1021/acs.analchem.5b00919

Gosalbo, L., Barrot, M., Fabriás, G., Aesequell, G. and Camps, F. (1993). Synthesis of deuterated cyclopropene esters structurally related to palmitic and myristic acids. *Lipids*, 28(12), 1125-1130. https://doi.org/10.1007/BF02537081

Guillen, M.D. and Ruiz, A. (2001). High resolution H-1 nuclear magnetic resonance in the study of edible oils and fats. *Trends in Food Science and Technology,* 12(9), 328-338. https://doi.org/10.1016/S0924-2244(01)00101-7

Hartmann, S., Minnikin, D.E., Römming, H.J., Baird, M.S., Ratledge, C. and Wheeler, P.R. (1994). Synthesis of methyl 3-(2-octadecylcyclopropen-1-yl) propanoate and methyl 3-(2-octadecylcyclopropen-1-yl) pentanoate and cyclopropane fatty acids as possible inhibitors of mycolic acid biosynthesis. *Chemistry and Physics of Lipids*, 71(1), 99-108. https://doi.org/10.1016/0009-3084(94)02315-8

Howard, D.W. (1991). A look at viscometry: viscosity

measurements help us understand flow behaviour. *Food Technology*, 45, 82-84.

Kadam, P., Vaidya, P., Mhaske, S., Int. J. and Adhes. A. (2014). Synthesis and characterization of polyesteramide based hot melt adhesive obtained with dimer acid, castor oil and ethylenediamine. *International Journal of Adhesion and Adhesives,* 50*,* 151-156. https://doi.org/10.1016/j.ijadhadh.2014.01.028

Ko, K.H., Park, H.R., Kim, J.S. and Kim, Y.W. (2013). Tangible plasticization/filler effects of sodium salts of dimer acids on the mechanical properties of styrene ionomers. *Journal of Applied Polymer Science*, 129(5), 2443– 2450. https://doi.org/10.1002/app.38836

Kouzu, M., Kasuno, T., Tajika, M., Sugimoto, Y., Yamanaka, S. and Hidaka, J. (2008). Calcium Oxide as a Solid Base Catalyst for Transesterification of Soybean Oil and Its Application to Biodiesel Production. *Fuel,* 87(12), 2798-2806. https://doi.org/10.1016/j.fuel.2007.10.019

Lee, S.J., Kim, Y.W., Yoo, S.H., Kim, N.K., Shin, J.H. and Yoon, B.T. (2013). Synthesis and Lubricating Properties of Dimer Acid Derivatives Based on Used Vegetable Oil Chemical. *Journal of the Korean Industrial and Engineering Chemistry,* 24(5), 530–536.

Li, Y., Ma, W., Qi, B., Rokayya, S., Li, D., Wang, J., Feng, H., Sui, H. and Jiang, L. (2014). Blending of soybean oil with selected vegetable oils: impact on oxidative stability and radical scavenging activity. *Asian Pacific Journal of Cancer Prevention*, 15(6), 2583-2589. https://doi.org/10.7314/APJCP.2014.15.6.2583

López-Varela, S., Sánchez-Muniz, F.J. and Cuesta, C. (1995). Decreased food efficiency ratio, growth retardation and changes in liver fatty acid composition in rats consuming thermally oxidized and polymerized sunflower oil used for frying. *Food and Chemical. Toxicology,* 33(3), 181–189. https://doi.org/10.1016/0278-6915(94)00133-9

Mallamace, F., Corsaro, C., Mallamace, D., Vasi, S., Vasi, C., Stanley, H.E. and Chen, S.H. (2015). Some thermodynamical aspects of protein hydration water. *The Journal of Chemistry Physics,* 142(21), 215103. https://doi.org/10.1063/1.4921897

Ohtsuki, T., Sato, K., Furusho, N., Kubota, H., Sugimoto, N. and Akiyama, H. (2013). Absolute quantification of dehydroacetic acid in processed foods using quantitative ^{1}H NMR. *Food Chemistr*y, 141(2), 1322–1327. https://doi.org/10.1016/j.foodchem.2013.04.005

Ohtsuki, T., Sato, K., Sugimoto, N., Akiyama, H. and Kawamura, Y. (2012). Absolute quantification for benzoic acid in processed foods using quantitative proton nuclear magnetic resonance spectroscopy. *Talanta*, 99, 342–348. https://doi.org/10.1016/j.talanta.2012.05.062

Owen, R.W., Giacosa, A., Hull, W.E., Haubner, R., Spiegelhalder, B. and Bartsch, H. (2000). The antioxidant/anticancer potential of phenolic compounds isolated from olive oil. *European Journal of Cancer,* 36(10), 1235-1247. https://doi.org/10.1016/S0959-8049(00)00103-9

Romero, A., Cuesta, C. and Sánchez-Muniz, F.J. (1998). Effect of Oil Replenishment During Deep-Fat Frying of Frozen Foods in Sunflower Oil and High-Oleic Acid Sunflower Oil. *Journal of the American Oil Chemists' Society*, 75(2), 161–167. https://doi.org/10.1007/s11746-998-0028-5

Romero, A., Cuesta, C. and Sánchez-Muniz, F.J. (2000). Cyclic fatty acid monomers and thermoxidative alteration compounds formed during frying of frozen foods in extra virgin olive oil. *Journal of the American Oil Chemists' Society*, 77(11), 1169–1175. https://doi.org/10.1007/s11746-000-0183-5

Sacchi, R., Patumi, M., Fontanazza, G., Barone, P., Fiordiponti, P., Mannina, L., Rossi, E. and Segre, A.L. (1996). A high-field H-1 nuclear magnetic resonance study of the minor components in virgin olive oils. *Journal of the American Oil Chemists' Society,* 73(6), 747-758. https://doi.org/10.1007/BF02517951

Sébédio, J.L. and Grandgirard, A. (1989). Cyclic fatty acids: natural sources, formation during heat treatment, synthesis and biological properties. *Progress in Lipid Research,* 28(4), 303–336. https://doi.org/10.1016/0163-7827(89)90003-9

Takeoka, G.R., Full, G.H. and Dao, L.T. (1997). Effect of heating on the characteristics and chemical composition of selected frying oil and fat. *Journal of Agricultural and Food Chemistry*, 45(8), 3244–3249. https://doi.org/10.1021/jf970111q

Talebian-Kiakalaieh, A., Amin, N.A.S. and Mazaheri, H. (2013). A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, 104, 683–710. https://doi.org/10.1016/j.apenergy.2012.11.061

Tseng, Y.C., Moreira, R.G. and Sun, X. (1996). Total frying use time effects on soybean oil deterioration and on tortilla chip quality. International Journal of Food Science and Technology, 31(3), 287– 294. https://doi.org/10.1046/j.1365-2621.1996.00338.x

Waltking, A.E. and Wessels, H. (1981).

Chromatographic separation of polar and non-polar components of frying fats. *Journal of the American Chemical Society*, 64(6), 1329-1330. https://doi.org/10.1093/jaoac/64.6.1329

Wang, S.N., Sui, X.N., Wang, Z.J., Qi, B.K., Jiang, L Z. and Li, Y. (2016). Improvement in thermal stability of soybean oil by blending with camellia oil during deep fat frying. *European Journal of Lipid Science and Technology*, 118(4), 524-531. https://doi.org/10.1002/ejlt.201500085

Wu, P.-F. and Nawar, W.W. (1986). A technique for monitoring the quality of used frying oils. *Journal of the American Oil Chemists' Society*, 63(10), 1363-1367. https://doi.org/10.1007/BF02679603

