UNIVERSITÀ DEGLI STUDI DI NAPOLI FEDERICO II

FACOLTÀ DI AGRARIA-PORTICI

DIPARTIMENTO DI SCIENZA DEGLI ALIMENTI

TESI DI DOTTORATO DI RICERCA IN

SCIENZE E TECNOLOGIE DELLE PRODUZIONI AGRO-ALIMENTARI

XXIV CICLO

EVALUATION OF NEW THERMO-OXIDATION MARKERS FOR OILS SUBMITTED TO PROLONGED AND DISCONTINUOUS FRYING.

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PREFACE

PREFACE

The deep fat frying, in its most general sense, includes all cooking operations where heat transfer occurs through fat and is one of the oldest food preparation processes.

Frying is a process of immersing food in hot oil with a contact among oil, air, and food at a high temperature of 150°C to 190°C (Choe & Min, 2007).

The color, aroma, texture and taste that this type of cooking is able to give food, are features that make it popular and widely used around the world. The typical fried foods are generated by chemical and physical transformations that occur in food and oil loading. During cooking, the food gives water and fat and assumes oil, at the same time complex chemical reactions develop, such as hydrolysis and thermal oxidation of fats.

These chemical reactions in frying oil produce volatile or non volatile compounds.

Most of volatile compounds evaporate in the atmosphere with steam and the remaining volatile compounds in oil undergo further chemical reactions or are absorbed in fried foods. The non volatile compounds in the oil change the physical and chemical properties of oil and fried foods. Non volatile compounds affect flavor stability and quality and texture of fried foods during storage.

Frying temperature and time, frying oil, antioxidants, and the type of fryer are the process variables that determine the predominance of a chemical reaction on the other, and thus the formation of the desired substances or that potentially harmful. In particular frying time increases the contents of free fatty acids (Mazza & Qi, 1992), polar compounds such as triacylglycerol dimers and oxidized triacylglycerols (Romero et al., 1998), dimers (Gordon & Kourimska, 1995), and polymers (Tompkins & Perkins, 2000).

High frying temperature accelerates thermal oxidation and polymerization of oils (Fedeli, 1988; Blumenthal, 1991; Tyagi & Vasishtha, 1996). High frying temperature decreases polymers with peroxide linkage and increases the polymers with ether linkage or carbon to carbon linkage. The intermittent heating and cooling of oils causes higher deterioration of oils than continuous heating due to the oxygen solubility increase in the oil when the oil cools down from the frying temperature (Clark & Serbia, 1991).

About quality of frying oil free fatty acids increase the thermal oxidation of oils, and their unsaturation rather than chain length led to significant effects on thermo-oxidative degeneration. Stevenson et al. (1984) and Warner et al. (1994) reported that the oxidation rate of oil increases as the content of unsaturated fatty acids of frying oil increases. In particular the content of linolenic acid is critical to the frying performance, the stability of oil, and the flavor quality of fried food (Liu & White, 1992).

The types of fryer affect the frying oil deterioration. Even and fast heat transfer to the oil can prevent hot spots and the scorch of oil. Polymerized fat deposited on the fryer causes gum formation, the formation of foam, color darkening, and further deterioration of frying oil. A small surface-to-volume ratio of fryer for minimum contact of oil with air is recommended for deep-fat frying.

In the study of the processes is necessary, however, distinguish between:

- Frying home, where the oil is used for a few minutes and only for a few cycles of frying;
- Fry in catering, where the activity is continued for several hours and repeated for several cycles;
- Frying in industry, where the operation is conducted continuously.

The main factors behind the continued expansion of fast food are to be found in two main aspects: on the one hand, the organoleptic and sensory characteristics possessed by only fried food, the other the relatively low cost of the trial conducted on a large scale. Therefore, despite the significant fat content of most fried foods and increasing consumers awareness of the correlation between health, food and nutrition in recent years, frying remains a major cooking method (Saguy & Dana, 2003). The quality of the oil used is of paramount importance in order to contain the reactions of oxidation, hydrolysis and polymerization that may occur during the frying operations. There are several studies conducted to evaluate the thermal stability of different types of frying oils (Bansal et al., 2010; Matthaus, 2007; Tabee et al., 2009).

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1. STATE OF THE ART

1.1 Frying process

Deep fat frying is an important, ubiquitous and highly versatile process, which has been used since antiquity to cook a wide spectrum of products (Blumenthal, 1996). In essence, frying is the immersing and cooking of foods in hot oil at a temperature above the boiling point of water. It involves heat and mass transfer and includes complex interactions between the food and the frying medium.
Basically, frying is a dehydration process with three distinctive characteristics (Saguy & Pinthus, 1995):
• High oil temperature (160-180 ° C) enables rapid heat transfer and a short cooking time;
• product temperature (except for the crust region) does not exceed 100°C;
• water-soluble compounds leaching is minimal.
Oil goes through approximately five phases as it is used for frying unless conditions are controlled to keep the oil in a state of equilibrium. In the first phase of the frying cycle, the oil is fresh, so oil during this time provides only a small amount of browning and food may look undercooked. Deep-fried flavor intensity of the food is usually also low because little oxidation has occurred. Frying operators often heat or fry in a fresh oil for a few hours to condition the oil. In the second phase of the cycle, the oil is at its optimum. Food has a desirable golden-brown color, is fully cooked, and has optimal deep-fried flavor. The low amount of oil oxidation that has occurred by this time is needed to provide the desirable deep-fried flavor in the food. Some oils will develop this characteristic deep-fried flavor more quickly than others depending on the linoleic acid content of the oil. During the third phase, the oil continues to deteriorate because of hydrolysis, oxidation and polymerization, leaving the oil lower in quality than at the second phase, but oil quality is still acceptable. Fried food at this phase will have a darker brown color and slight off-flavors may be detectable in the food. By the fourth phase, the oil has deteriorated even further and oil quality is marginal. Food has a dark-brown color and moderate-to-strong off-flavors; and the oil will probably foam. Foaming prevents uniform cooking of the food, so the fried food may not be fully cooked. By the time the oil reaches the fifth and final phase of its fry life, severe oil degradation has occurred. Foaming of the oil is a major problem, and fried food has unacceptable flavors and may not be fully cooked in the center because foaming of the oil has limited direct contact of oil and food. Unless frying conditions are adjusted to maintain the oil in the second phase of the cycle, the oil will continue to deteriorate and may have to be discarded.
For all these reasons, the frying is a process more difficult to understand because of the multitude of physical and chemical changes that occur and the complexity of the products that are formed. This complexity lies in the progressive deterioration of the oil led to high temperatures, causing continuous changes in the composition of the food is fried in the frying bath. Also, during frying, many other reactions occur, such as gelatinized starch, a Maillard reaction, the denaturation of proteins and the decrease in humidity, which is manifested by swelling of the product, the formation of a thin crust, the appearance of a golden color, good texture and a pleasant smell of fried food (Kochhar & Gertz, 2004).
Unfortunately, alongside the positive attributes taken from food fried, also physical and chemical unwanted changes occur in packing of the frying, with the formation of compounds more or less harmful to health. The food absorbs the oil, more or less degraded, which also affects the quality of dietary fat, and in general the quality of the finished product (Dobarganes et al., 2000).

1.2 Physical changes

The deep fat frying process is complex operation involving high temperatures, significant microstructural changes both to the surface and body of the food being fried, and simultaneous heat and mass transfer resulting in flows in opposite directions of water vapors and oil. The events occurring during frying of food are shown below:

- oil temperature decrease during the dive of food in hot oil and subsequent increase,
- modifications to detriment of the components present in food (denaturation of protein and starch gelatinization, etc.),
- steam formation by water contained in food ,

- dehydration of surface food and crust formation,
- oil absorption by the food,
- oil thermo-oxidation.

The simplified scheme of the heat and mass transfer operation during the actual frying of food is illustrated in **Fig. 1.1** (Kochhar & Gertz, 2004).

1.2.1 Heat transfer during deep-frying

First, the frying process involves a transfer of heat; we can assume the presence of two regions separated by an imaginary interface: the crust and the core. Heat is transmitted from hot food to the outer surface during natural convection heating. When the surface reaches 100 ° C, the water begins to evaporate and we are witnessing the formation of the crust. The transformation of water into steam requires thermal energy is supplied from the oil around, so its temperature undergoes an immediate lowering. The water vapor generates flows out through the surface of food with minimal resistance, so the heat from the oil to the crust is taken for forced convection (Farid & Chen, 1998). The greater amount of heat transmitted is used to evaporate the water, while the remaining small amount is used to a significant increase in the temperature of the food that does not exceed 100 ° C, avoiding a possible charring of the food itself that could occur at temperatures of action of the oil bath (Blumenthal, 1991). Finally, the heat is transmitted by conduction from the interface towards the core imaginary. This last stage of the process is essentially tied to water that among the constituents of the food, is the most efficient conductor of heat (Orthoefer et al., 1996).

The cooking time is relatively short by frying: two thirds correspond to the evaporation phase where the temperature inside the food itself remains very close to 100 ° C, and the remainder corresponds to the action of hot fat. The real-time action of fat on the food is therefore minimal, so the attack on thermolabile components of the food is less than other cooking techniques.

1.2.2 Mass transfer during deep-frying

Next to the heat transfer we find the mass transfer involving the oil and moisture.

The mass transfer evolves through two mechanisms:

1) adsorption of the first oil to replace evaporated water;

2) second adsorption process, which occurs primarily when frying is completed.

In the first phase, reaching a temperature of 100 ° C, occurs the evaporation of water contained in the surface layers of the product. The changes in the cellular structure of food products, for the formation of pores due to evaporation of water, allow the oil to penetrate into the gaps created. In fact, when the water becomes steam, it escapes from the product, leaving a network “sponge like”, so the oil passes through these channels, which allows its penetration during the first 20 seconds of frying (Moreira et al., 1997).

In later times, the temperature of the food increases and the moisture still trapped inside, it is converted into steam causing a pressure gradient. The steam escapes through the capillaries and the channels of the cellular structure, whereby the oil adheres to the surface of the food or penetrates into the gaps created by the water is literally pushed out. So the steam generated prevents the further penetration of the oil in the interstices. The movement of oil, at this stage can be described as a process of advance and retreat, dependent primarily on the vapor pressure and the nature of the capillaries.

Once the fried product is removed from hot oil and begins to turn colder, the vapor pressure decreases due to condensation inside, creating a "vacuum effect". The oil is confined to the surface region of the fried product and located in the pores of the crust, involving a limited group of cells, and advances in the product. The oil penetration is limited to approximately 1 mm, so it is essentially a phenomenon on the surface, the result of a competition between drainage and suction in the pores of the crust (Keller et al., 1986, Bouchon & Pyle, 2005). Consequently, the microstructure of the crust, formed during frying, is the most important factor determining the quantity of oil in the final fried product.

The evolution of mass transfer during frying explains the three locations observed in a fried food: structural oil (absorbed during frying), which represents 20% of the total, surface oil and surface oil absorbed (during cooling) (Moreira et al., 1997).

The explicit phenomena clearly demonstrate that the penetration of the oil and the spill of water are not synchronized phenomena, adsorption also depends on several factors, some of which are closely linked to the same process as the temperature and duration of frying, which determine the amount of water removed and the ways in which moisture is lost, while others are related to food properties such as shape, composition, or changes undergone by the product during the treatment, in particular the rate of formation of the crust (Orthoefer et al., 1996).

It has been found that temperature has no significant effect between 150 and 180°C although, in general, the higher the temperature the lower the oil absorption on the surface and, on the contrary, an excess of oil

absorption may result from low frying temperatures. Interrelation of both variables in frying is common and thus, the higher the temperature the shorter the time to obtain a fried product of similar quality. Apart from the time/temperature parameters, mass transfer depend on both food and frying oil. With respect to the food, many variables affect the final composition of the finished fried product. Among them, food composition, in particular the surface structure and composition, moisture, lipid content, product shape, surface-to-weight ratio, porosity, and pre-frying treatment have been reported (Fillon & Henry, 1998; Saguy & Pinthus, 1995).
In general, oil absorption depends on the frying oil quality more than on the oil or fat used for frying. Influence of oil quality was attributed to formation of degradation compounds which increase the polarity of the frying medium. On the one hand, the oil viscosity increases, which in turn could contribute to increase the amount of oil on the food surface (Alim & Morton, 1974), and, on the other hand, the interfacial tension between the food and the oil would decrease, thus facilitating oil absorption (Dobarganes et al., 2000).
From a quantitative point of view, used frying oils are mainly affected by contamination with fats or lipids, which migrate to the frying medium from foods. Two different types of fatty foods will be considered separately:

- naturally fatty foods which are normally coated by batter or bread and are characterized by a low content of lipids on their surface;
- the increasing group of frozen pre-fried foods (potatoes, fish, vegetables, etc.) where the fat or oil is mainly located on the surface.

Lipid exchanges in frozen pre-fried products are of special interest as the lipid constituents have two specific characteristics:

- pre-fried products contain significant amounts of absorbed used frying fat or oil of unknown composition and quality depending on the variables of the pre-frying process.
- as a consequence of the previous frying process, the oil is preferably absorbed in the external layers of the food and thereby lipids are in contact with the frying oil during the second frying operation.

Fat absorption, lipid interchange, and possibilities of preferential absorption of polar compounds on food surface during frying of frozen pre-fried foods have been studied in details. Fat absorption clearly depends on the type of food while similar levels of polar compounds, polymers, and minor compounds were found in the lipids extracted from fried foods and in the frying oils. On the other hand, similar fatty acid profiles were found for the oil and the food fried in it, indicating that lipid interchange was very high. In fact, more than 90% of the fried food lipids came from the frying oil while more than 85% of the pre-fried food lipids were released into the frying oil (Dobarganes et al., 2000).
The main originality of deep frying is to transfer heat at a very high rate using the heat reservoir created by the large volume of oil compared with the product.
Due to the density and heat capacity of oil, involved heat transfer rates are in particular higher than those encountered with other heat vectors such as gas (e.g., hot air, superheated steam). Besides, when the product is surrounded with oil (immersed product), heat is transferred almost uniformly to the product. This feature is more difficult to achieve with alternative cooking or drying processes such as pan-frying and infrared heating. Deep frying uses a large volume of liquid with a high boiling point, such as oil and fat, whose initial temperature is set significantly above the boiling point of free water. This process can be done in batch or in continuous form using an immersed conveyor. Because oil and fats are highly thermo-expandable fluids, buoyancy forces are particularly efficient to homogenize the temperature along the vertical direction. Steam bubbles escaping from the product external surface are observed immediately or a few seconds after immersion into hot oil. Because steam is then the only gas phase in the product, vaporization of free water occurs at the saturation temperature of water, noted *T*sat, and the vaporization rate is roughly proportional to the temperature difference between the oil bulk and *T*sat.
In the first phase of frying, from immersion of the product until surface temperature equals to the boiling point, the natural convection flux dominates the heat transfer from frying medium and it' s characterized by three regimes. The very early first transitory regime (regime A) is associated with very high convective heat fluxes and is followed by a slug flow of steam bubbles. When the generation of steam is faster than the ability of the medium to remove steam, the convection flux decreases due to the heat transfer resistance by steam film around the product.
Because the core temperature remains below the saturation temperature, the initial vaporization regime is related to the surface vaporization of water. The second regime (regime B) corresponds to an almost constant heat flux and a core temperature close to *T*sat. During regime 2, water is vaporized inside the product. The third regime (regime C) coincides with an increase of the core temperature above *T*sat and a decreasing flux. The initial superficial vaporization (regime A) and subsequent in-depth vaporization during regime B creates a porous dried region and overheated region (heated above *T*sat), which is generically called "crust". Main organoleptic characteristics (texture, color, aroma) are generated in the crust. During the same period and according to the geometry, the core temperature remains below or close to *T*sat. The core contains free or capillary water, but it remains undifferentiated and soft. The main transformations which occur in this region are starch gelatinization and protein denaturation, and they participate in increasing the digestibility of fried food. French fries are removed from oil during regime C, whereas chips are removed after regime C. Several experimental results have

demonstrated that liquid water transport has a significant role during frying. It is responsible for cooling of the product surface during regime B (beginning of stage 2) and preserves the product from rapid overheating and darkening (Vitrac et al., 2002; Vitrac et al., 2003).
Generally the oil uptake occurs mainly during cooling immediately after frying.
Reduction of oil uptake is the main concern of researchers who wish to satisfy the health demands of consumers. Coating of potatoes with hydrocolloids and/or modified starches is an alternative way to reduce oil uptake during frying. Incorporation of powdered cellulose or cellulose derivatives into batters or doughnut mixes reduces oil uptake due to their thermal gelatinization and film-forming properties. In addition, alternative frying technologies such as vacuum, pressure or microwave frying to reduce the oil content of these products appear promising.

1.3 Chemical changes

During heating or frying processes, edible oils undergo a complex series of reactions such as autoxidation, thermal polymerization, thermal oxidation, isomerisation, cyclisation and hydrolysis (Kochhar & Gertz; 2004). At elevated temperatures, when the oxygen supply is rather limited (as in the case of "steam blanket" generated on the oil surface by water which evaporated from the fried food), the main reactions lead to polymerization rather than oxidation (Gertz et al., 2000). It has been observed that the chemical reactions under simulated frying conditions are different from those taking place during heating without food and from those formed at room temperature. This means that under frying conditions, the decomposition of fat is caused not only by hydrolytic and radical-induced reactions, but also possibly by non-radical reaction pathways (Brutting & Spiteller, 1994).
Table 1.1 summarizes the three main groups of compounds, volatile and non-volatile, which arise during the frying, when oil or fat are subjected to high temperature, about 180 ° C in the presence of air and moisture. In addition, the reactions of fried oils with proteins and carbohydrates that make up food, give desirable and not desirable flavors. The first are necessary for fried foods because contribute to their organoleptic characteristics, the second (off-flavors) are derived from extensive thermal degradation processes that occur during prolonged frying time (Frankel, 1998).

1.3.1 Hydrolytic alteration

When food is fried in heated oil, the moisture forms steam, which evaporates with a bubbling action and gradually subsides as the foods are fried. Water, steam, and oxygen initiate the chemical reactions in the frying oil and food. Water, a weak nucleophile, attacks the ester linkage of triacylglycerols and produce di- and mono-acylglycerols, glycerol, and free fatty acids. Free fatty acids and their oxidized compounds produce off-flavors that make the oil less acceptable for deep fat-frying.
Although the hydrolysis is one of the simplest reactions that occur during frying, there are conflicting results in the literature. For some authors, the hydrolysis is the most important reaction that occurs during frying (Pokorny, 1999), while for other ones, products of hydrolysis can be considered of minor importance compared to the wide range of new compounds formed (polar compounds , polymerized triacylglycerols), although the food substrate has a high water content. Apparently, it seems that fatty acids are lost during the distillation process. Therefore, quantification of diglycerides is often preferred to the analysis of fatty acids to assess the contribution of the hydrolysis reaction, because these compounds are held in the frying oils (Dogarbanes et al., 1996). Although free fatty acids thus formed are oxidized more rapidly and promote thermal oxidation by dissolving the metal catalysts, the water steam, covering the surface of the frying oil, reduces the availability of oxygen in the air and then the speed of oxidation. The steam removes the volatile decomposition products, slowing the decomposition of the oil.

1.3.2 Oxidative alteration

Oxidation has a significant financial impact due to the development of rancid flavors that reduce the organoleptic characteristics, and the formation of oxidized products that may cause a health hazard.
If you look at the phenomena more closely and analyze the causes, four factors are important:
• the presence of oxygen;
• the unsaturation of the oil;
• the presence of metals;
• process temperatures used.

The factor "presence of oxygen", confirms, of course, that it is an oxidation reaction, favored by the reactivity of the compound. Oxygen, along with the air, that includes it, can come the oil in various ways: it can be dissolved in oil or be present in the headspace of the container.
The factor "unsaturation" of oil has a great influence on the oxidation; this is all the more evident the higher is the content of unsaturated fatty oil.
The "presence of metals" promotes the oxidation reaction, because the metals, though present in trace amounts, act as catalysts through complex mechanisms of transport charges. The use of discs of iron in the extraction system for pressure, or metal containers in which the internal welds or surfaces in contact with oil are not inert, can promote oxidative rancidity. Finally, the '"radiation" is an important factor in the autoxidation, especially from a UV light source, characterized by a shorter wavelength (up to 390 nm).
Autoxidation is the direct reaction of molecular oxygen with organic compounds under mild conditions. Oxygen has a special nature in behaving as a biradical by having two unpaired electrons (˙O-O˙) in the ground state and is said to be in a triplet state. The oxidation of lipids proceeds like that of many other organic compounds by a free radical chain mechanism, which can be described in terms of initiation, propagation, and termination processes. These processes often consist of a complex series of sequential and overlapping reactions.
The direct attack of atmospheric oxygen on the chain of unsaturated fatty acid is one of the points that raises more questions and seems to be thermodynamically unlikely, because the reaction has very high activation energy (35 to 65 kcal/mole).
The direct oxidation of unsaturated lipids by triplet oxygen ($^3O_2$) is spin forbidden because the lipid ground state of singlet multiplicity has an opposite spin direction from that of oxygen of triplet multiplicity.
Because the reaction becomes possible, it is necessary that oxygen, which enters the reaction, is in the state of singlet multiplicity. The oxygen in the singlet state can be formed through a photochemical reaction in the presence of a "sensitizer" can be like the chlorophyll in olive oil.

Iniziazione

$$LH \xrightarrow{\text{Catalizzatore}} L\cdot + H\cdot \qquad (1)$$

Propagazione

$$L\cdot + O_2 \longrightarrow LOO\cdot \qquad (2)$$

$$LH + LOO\cdot \longrightarrow L\cdot + LOOH \qquad (3)$$

$$LOOH \longrightarrow LO\bullet \qquad (4)$$

Terminazione

$$L\cdot + L\cdot \longrightarrow L\text{-}L \qquad (5)$$

$$LO\bullet + L\cdot \longrightarrow LOL \qquad (6)$$

$$LOO\cdot + L\cdot \longrightarrow LOOL \longrightarrow 2LO \longrightarrow LL + LOL \qquad (7\text{-}10)$$

The formed radicals interact with oxygen in a very fast reaction. The alkyl radicals (L·), formed in reaction (1), tend to accumulate as the reaction rate of oxygenation (2) decreases. The termination reaction (5-10) acquires more importance because of condensation reactions between alkyl radicals, with formation of stable high molecular weight products.
A modern exposition of oxidation mechanism of polyunsaturated fatty acids focuses on the presence of allylic hydrogens, i.e. the hydrogen atoms linked to carbon atoms adjacent to double bonds (Nawar, 1996). A fatty acid with a double bond has four allylic hydrogens, as shown below:

-C-H_2C-C=C-CH_2-C-

The allylic hydrogens have relatively low energy of dissociation and can be quickly removed, so as to form a free radical (L·). The formation of free radical is the first step in the oxidation chain reaction. The allyl radical that is formed

HC-C=C·

reacts with oxygen to form a peroxyl radical (LOO·). The peroxyl radical may react with an "available" hydrogen atom (LH), forming another free radical (·L) and a hydroperoxide (LOOH). The hydroperoxide formed

during oxidation may subsequently decompose, generating additional free radicals and/or secondary oxidation products that accumulate and contribute to increase oil rancidity.
Polyunsaturated fatty acids (PUFAs) have a greater number of allylic hydrogens. In addition, fatty acids such as linoleic, linolenic or other PUFA have a diallylic ethylene group able to lose faster an hydrogen atom.
The classical mechanism for the free radical oxidation of methyl oleate involves hydrogen abstraction at the allylic carbon-8 and carbon-11 to produce two delocalized three carbon allylic radicals (**Fig. 1.2**). According to this mechanism, oxygen attack at the end-carbon positions of these intermediates producing a mixture of four allylic hydroperoxides containing OOH groups on carbons 8, 9, 10 and 11, in equal amounts:
9-hydroperoxy-trans-10-octadecenoate (trans-9-OOH)
11-hydroperoxy-cis-9-octadecenoate (cis-11-OOH)
10-hydroperoxy-trans-8-octadecenoate (trans-10-OOH)
8-hydroperoxy-cis-9-octadecenoate (cis-8-OOH)
Linoleate is 40 times more reactive than oleate, because it has an active bis-allylic methylene group on carbon-11, between two double bonds that can lose a hydrogen atom very readily. Hydrogen abstraction at the carbon-11 position of linoleate produces a hybrid pentadienyl radical, which react with oxygen at the end carbon-9- and 13-hydroperoxides (**Fig. 1.3**). The greater reactivity of linoleate to autoxidation is due to the formation of a pentadienyl radical intermediate, which is more effectively stabilized by resonance, and the resulting dienoic hydroperoxides produced that are stabilized by conjugation. These isomeric conjugated dienoic hydroperoxides are a mixture of four cis, trans and trans, trans conjugated diene hydroperoxides:
9-hydroperoxy-trans-10, cis-12-octadecadienoate (cis, trans-9-OOH)
9-hydroperoxy-trans-10, trans-12-octadecadienoate (trans, trans-9-OOH)
13-hydroperoxy-cis-9, trans-11-octadecadienoate (cis, trans-13-OOH)
13-hydroperoxy-trans-9, trans-11-octadecadienoate (trans, trans-13-OOH)
Methyl linolenate has two bis-allylic methylene groups and reacts twice as fast with oxygen as linoleate. The two bis-allylic methylene groups in linolenate act independently and are not activated by each other. By the same mechanism as linoleate, two pentadienyl radicals are formed by hydrogen abstraction on carbon-11 and carbon-14 between the two 1,4-diene systems on carbon-9 and carbon-13 (**Fig. 1.4**), on one hand, and on carbon-12 and on carbon-16, on the other. Reaction with oxygen at the end-carbon positions of each pentadienyl radical produces a mixture of four peroxyl radicals leading to the corresponding conjugated diene 9-, 12-, 13- and 16-hydroperoxides containing a third isolated cis double bond:
9-hydroperoxy-trans-10-, cis-12, cis-15-octadecatrienoate (trans, cis, cis-9-OOH)
13-hydroperoxy-cis-9, trans-11, cis-15-octadecatrienoate (cis, trans, cis-13-OOH)
12-hydroperoxy-cis-9-10, trans-13, cis-15-octadecatrienoate (cis, trans, cis-12-OOH)
16-hydroperoxy-cis-9-10, cis-9, trans-14-octadecatrienoate (cis, cis, trans-16-OOH)
It is good to clarify that, in addition to geometric isomerization, the PUFAs auto-oxidation can cause a positional isomerization, all the hydroperoxides formed possess conjugated double bonds.
Following their training, the hydroperoxides, for instability, begin to decompose, this occurs at temperatures above 80 ° C, for which, at high temperatures of frying, the induction period is zero. At this point the hydroperoxides undergo spontaneously and quickly decomposition, giving rise to a variety of secondary oxidation products (Frankel, 1998). Compounds produced by decomposition of hydroperoxides include alkanes, alkenes, aldehydes, ketones, short chain fatty acids, carbonyl compounds such as hydroperoxy, and epoxy-hydroxy acids (Chang et al., 1978).
While the hydrolysis reactions release compounds with known structures, such as diacylglycerols, monoglycerides and fatty acids, oxidative reactions generate a large amount of new volatile and non-volatile compounds. Of particular interest in the chemical and nutritional frying is the formation of non volatile degradation compounds, which remain in the oil absorbed by the food matrix, and then ingested. Considering the number of oxygenated forms in one or more fatty acids and triacylglycerols, and their several combinations, it can imagine the variety of oxidized compounds with similar molecular weight to the starting triacylglycerols, including epoxy fatty acids, ketones and hydroxylic fatty acids esterified with the glycerol backbone of triacylglycerol involved. In **Fig. 1.5** the mechanism of formation of these compounds is shown. (Capella, 1989).
The hydroperoxides degradation results in the formation of short-chain fatty acids, which remain attached to the skeleton of glycerol to form a non-volatile part of the molecule.
The **Fig. 1.6** summarizes the formation of short chain compounds attached to glycerol, by the 9-hydroperoxide of oleic, linoleic and linolenic acids. The main components are the C9 acid, C9 aldehyde, formed in oxidized triacylglycerols, and lower the amount of C7 and C8 aldehydes, probably formed by breaking of 13-hydroperoxide of linoleic acid and by 8-hydroperoxide of oleic acid (Marquez-Ruiz & Dobarganes, 1996). The short-chain unsaturated fatty acids could also be formed from 13-hydroperoxide of linolenic acid and from 10-/11-hydroperoxide of oleic acid, but this mechanism is unlikely. Therefore, among short-chain fatty acids linked to glycerol of the triacylglycerols, the C7 and C8, respectively derived from 8 - and 9-hydroperoxide of the main unsaturated fatty acids, are the compounds most likely found.

Studies on model systems showed that especially methyl octanoate is one of the most significant products of oxidation of fatty acids methylesters. Since short-chain fatty acids are attached to the glyceridic skeleton forming a part of the molecule non-volatile, the quantification of this short-chain fatty acid is an indirect measure of oxidation and of formation of volatile compounds.

1.3.2.1 Volatile compounds

There are three major sources of flavor in frying oils. First, naturally occurring flavor compounds in oils give distinct flavors to all oils. These distinct flavors are most noticeable after the oil is extracted or expelled from the oilseed. Many oils are refined and deodorized to remove all or most of these flavors. Other oils such as olive oil are pressed without further processing so the natural flavor of the oil is evident. On the other hand, some oils such as corn and peanut are processed to leave some of the natural positive flavors in the oil. In some countries, such as the USA, peanut oil is used for fried snack foods because of its unique and desirable nutty flavor. Processing of oil can also affect frying oil flavor. For example, when oil is hydrogenated, it develops a specific flavor that is often described as fruity, flowery, and/or milky. The greater the degree of hydrogenation, the more distinct this flavor becomes. Finally, the primary source of flavor in frying oils comes from the decomposition of the major fatty acids, oleic, linoleic, and linolenic at temperatures of approximately 180°C.

During frying, a large mixture of volatile substances is produced by rapid decomposition of hydroperoxides and polyunsaturated aldehydes. These volatile decomposition products are found in relatively small amounts, because a large portion is removed from the oil by steam distillation and the sweeping action of steam generated during frying. The remaining volatile compounds are of concern, because they are partially absorbed by the fried foods and contribute to their flavor and to the odor of the room where frying is carried out, also referred to as room odor. Volatile compounds produced by thermal oxidation include aldehydes, ketones, alcohols, acids, esters, hydrocarbons, lactones, substitude furans, and aromatic compounds. Gas chromatographic analyses of fat samples after different frying treatments represent mainly the more stable volatile compounds remaining in the fats.

These compounds are generated primarily through a mechanism of homolytic β-scission of alkoxy radicals formed from each of the different fatty acid hydroperoxides. The reaction mechanism is shown in **Fig. 1.7**. The products of β-scission of oleic and linoleic acid hydroperoxides are shown in **Tab. 1.2.** The unsaturated aldehydes (2-alkenals and 2,4-alkadienals) can be further decomposed: the O_2 can attack the C2 of 2-alkenals and produce a very reactive double radical, which can interact with two molecules of fatty acid (RH), and become alkanal-hydroperoxide (also producing two alkyl radicals • RH), which can still decompose giving a saturated aldehyde (with two carbons less than to the starting unsaturated aldehyde) and a dialdehyde. The 2,4-alkadienals are subjected to the same attack, giving rise to 2-keto-4-alkenals or 2-hydroxy-4-alkenals.

The major volatile compounds are found in both frying oils and in fried foods derived from the decomposition of lipid oxidation products and include 1-pentanol, furfuryl alcohol, trans-2-heptenal, 5-methylfurfural, 1-octen-3-ol, octanal, 2-pentylfuran, trans-2-nonenal and hexadecanoic acid. Additional minor volatile compounds are found in both frying oils and in fried foods, including:

- cis, trans and trans, trans-2,4-decadienal derived from oxidized linoleate
- 2,4-heptadienal derived from linolenate

The isomers of 2,4-decadienal impart a desirable fried food flavor in fried potatoes when present in small amounts, but excessive amounts of this aldehyde would be expected to cause undesirable rancid flavors.

In addition to the frying oil, other sources of volatiles include oxidative and thermal decomposition of the lipids in the food itself; breakdown products of certain non-lipid food components (e.g. amino acids); and the interaction among these products and/or with other food components (e.g. phospholipids, proteins). The Maillard reaction, involving reducing sugars and amino acids, results in a wide range of compounds including sulfur and nitrogen (methylpyrazine and 2,5-dimethyl pyrazine in potatoes) and furfurals that are formed as secondary products of Strecker degradation between α-dicarbonyl compounds and aminoacids (Frankel, 1998).

Many of the volatile decomposition products formed during frying volatilize and/or further decompose, so it is difficult to get an accurate measure of oil deterioration by instrumental and chemical analysis of these compounds. Methods that measure volatile compounds directly or indirectly include gas chromatographic volatile compound analysis and sensory analysis. These methods are better for measuring the quality and stability of the fresh and aged fried food than for measuring the quality of the frying oil. Gas chromatographic volatile compound analysis measures compounds that are directly related to the flavor of the fried food. Identifying volatile compounds in fried food is important because these compounds help in understanding the chemical reactions that occur during frying, and because the flavor of deep fried food is caused by the volatile compounds. Although the volatile compounds in the frying oil are continually changing, measuring these compounds in the frying oil can give some indication of oil deterioration, but care should be taken in interpreting data on volatile compounds in used frying oil because of the fluctuations in formation and degradation of the compounds at frying temperature. Gas chromatography–mass spectrometry (GC/MS) can be used to identify

volatile compounds in frying oils, such as hydrocarbons, aldehydes, alcohols, furans, esters, ethers, acids and lactones. Volatile compounds can be identified and quantified from fresh and aged fried food more reliably than in the frying oil. Sensory evaluation of fried food is a good method to determine when to discard frying oil. Scientific groups in Germany use sensory assessment of frying oils; however, if assessment does not give a clear indication that the oil is deteriorated, instrumental or chemical analysis is used to support a final decision on oil quality. The Third International Symposium on Deep-Fat Frying recommended that sensory parameters of the fried food be the principal quality index for deep fat frying. Sensory analysis of frying oil and fried-food quality may be conducted by analytical descriptive/discriminative panels using trained, experienced panelists or by consumer panels using untrained judges. However, results from consumer panels that measure the flavor likeability of food are usually dependent upon individual likes and dislikes, rather than objective standards used by trained panels. Consumer panels may find no differences in fried food flavors, whereas a trained, experienced analytical descriptive panel can usually detect significant differences in the type and intensity of flavors in fried food prepared in various oil types.

The general factors that help inhibit frying oil deterioration include choosing fresh oil with good initial quality that has no prior oxidation and low amounts of catalyzing metals. The extent of the degradation reactions of hydrolysis, polymerization and oxidation can be controlled by carefully managing frying conditions, such as temperature and time, exposure of oil to oxygen, continuous frying, oil filtration, turnover of oil, and addition of citric acid, antioxidants and/or anti-foam agents. As discussed previously, the fatty acid composition of the frying oil has a major effect on the flavors in the oil and fried food. Therefore, modifying the fatty acid composition will help to control the flavor development in the oil. Hydrogenation, one of the first tools that oil processors used to control flavor development in frying oils, increased oleic acid and decreased linoleic acid and linolenic acid. However, hydrogenation produces *trans* fatty acids that are not healthful, and it also contributes a distinct flavor that is not acceptable to some food manufacturers. Plant breeding for specific fatty acid compositions is another alternative to control flavor in oils. Since the mid-1980s, plant geneticists have modified fatty acid compositions by plant breeding techniques. Based on over 50 years of edible oil stability research, the targets for modifying fatty acid compositions of oilseeds by plant breeding were identified as lower linolenic acid, lower linoleic acid and higher oleic acid. The research on oils with reduced linolenic acid was an early objective and resulted in liquid salad oils with increased oxidative stability (Liu & White, 1992a; Miller & White 1992; Mounts et al., 1988). In other reports, oils with high amounts oleic acid and/or lower levels of linolenic acid had improved stability to degradation during the frying compared to their unmodified counterparts of sunflower, corn, soybean, and canola (low erucic acid rapeseed) oils (Eskin et al., 1989; Liu & White, 1992b; Mounts et al., 1994; Warner & Knowlton, 1997; Warner & Mounts, 1993). However, frying studies that included chemical and sensory analyses of the fried food and oils determined that as the amount of oleic acid was increased with corresponding decreases in the amount of linoleic acid, the quality and intensity of the deep-fried flavor of the fried food decreased (Warner & Knowlton, 1997; Warner & Mounts, 1993; Warner et al., 1997; Warner et al., 1994). In addition, these high oleic acid oils also produced increased intensity levels of undesirable aromas such as fruity, plastic, acrid, and waxy at high temperatures.

Frying operators can optimize the flavor development in their frying oils and fried food by the fatty acid compositions they select. For example, Cargill, a major oil producer in the USA market, produces two types of high oleic/low linolenic acid canola oils. One of these oils, "Clear Valley 75", has 75% oleic acid and 12% linoleic acid, and is sold for high-stability uses and is described as delivering a neutral flavor. On the other hand, "Clear Valley 65" has 65% oleic acid and 22% linoleic acid, and is described as providing superior stability and improved fried flavor in the food.

1.3.3 Thermal alteration

The oxidation of unsaturated fats is not only greatly accelerated at high temperature, but the free radical mechanism is changed by the decrease in oxygen concentration in heated fats. At elevated temperatures, the oxygen availability is lower and becomes limiting.

The alkyl radicals, formed by initiation, become more important because the rate of the oxygenation reaction is diminished at elevated temperatures. At temperatures above 100°C, the initial hydroperoxides decompose rapidly into a multitude of volatile and non-volatile products (Frankel, 1998).

Two mechanisms have been postulated for the thermal oxidation of unsaturated fats:

- Thermal decomposition by direct interactions of radicals, when unsaturated fats are continuously heated at elevated temperatures,
- Induced decomposition through the intermediacy of hydroperoxides, when unsaturated fats are subjected to intermittent heating.

Under these conditions, hydroperoxides accumulating at the lower temperatures contribute more radicals by decomposition when the fats are reheated. Intermittent heating of unsaturated fats is generally assumed to be more destructive than continuous heating.

1.3.3.1 Cyclic monomers

During heating of vegetable oils at temperatures of about 200 ° C, the formation of cyclic fatty acids, mainly from linoleic (**Fig. 1.8**) and linolenic (**Fig. 1.9**) acids occur.
Main structures include disubstituted five-membered (cyclopentyl) and six-membered (cyclohexyl) compounds with unsaturation inside and outside the rings. Although a mechanism suggested for these cyclizations may involve intramolecular rearrangements catalyzed by traces of hydroperoxides as initiators, another non-radical pathway may proceed by Diels-Alder cyclization of conjugated diene intermediates (Frankel, 1998).

1.3.3.2 Polymeric compounds

The predominant group of non-volatile compounds formed during frying of unsaturated fats includes dimers and oligomers. These high molecular weight compounds are mostly formed in the termination stages of free radical oxidation.
The oil viscosity increases as polymers increase in the frying oil. The compounds formed by the polymerization may be useful as precursors of off-flavor. Used frying oils and even fried foods have a larger quantity of off-flavor, like smell and burned.
During frying three different types of dimers can form:

- non-polar dimers: R–CH=CH• + R• $\longrightarrow$ R–CH=CH–R
- polar dimers: R–CH=CH• + •OH $\longrightarrow$ R–CH=CH–O– R
- oxygenated polar dimers: R–(OH)–HC• + R• $\longrightarrow$ R–(OH)–HC–R

Polar dimers are oxygenated and form either by combining radicals containing alkyl and alkoxyl radicals and linked by ether bonds (C-O-C), or by combining radicals containing oxygenated functions (hydroxy, keto, epoxy). Polar dimers linked by peroxy bonds (C-OO-C) are only formed at low temperatures and decompose at elevated temperatures (above 100°C). The polar dimers structures remain not clear. The difficulty is mainly due to the heterogeneity of this group of compounds: the different oxygen functions may be present in oxidized monomers before the formation of dimers, or generated by oxidation of the non-polar dimers, and then, more than one functional group may be present in the same dimeric molecule. Finally, oxygen may or may not be involved in the binding of the dimers. Consequently, the large number of possible combinations of polar dimers is a complex mixture difficult to separate.
Non polar dimers are formed by addition of alkyl radicals and linked by carbon-carbon bonds. According to the type of fatty acid precursors these carbon-carbon dimmers include monoene, diene and tetraene structures.
At high temperatures there is also a non-radical polymerization by Diels-Alder reactions between two fatty acids with conjugated double bonds, or between a fatty acid with two conjugated double bonds and one with non-conjugated double bonds to form a substituted cyclohexene (**Fig. 1.10**).
The dimerization of unsaturated fatty acids can also start with a cationic mechanism, which intermediate is stabilized with a mesomeric effect, leading to the formation of a dimer with a CC bond and a possible cyclization (Kochhar & Gertz, 2004).
More complex structures have been identified in oils used after frying, including unsaturated bicyclic compounds with conjugated and non-conjugated double bond, trimers, cyclic polar dimers, and tetrahydrofuran tetrasubstitude dimers. These polar and non-polar dimeric and oligomeric compounds are not completely characterized because of their complex composition (Frankel, 1998).

1.4 Factors affecting the quality of il during deep-fat frying

Fats degradation during frying depends on a combination of various factors, such as the oil characteristics and the manner in which the oil is handled and treated (Frankel, 2005).
The main factors that affect the deterioration of oil during deep-fat frying are:

- turnover rate of oil and replenishment with fresh oil
- frying time and temperature
- initial oil quality
- composition of food to be fried
- filtration

- antioxidants

1.4.1 Replenishment of fresh oil

This refers to the amount of fat added to the kettle to make up for the amount removed by the food during frying. The turnover rate is an important factor for the control of frying oil condition. Stevenson et al. (1984) recommend a daily turnover of 15% to 25% of the capacity of the fryer. The absorption of fat by the food during frying increases with the increase in viscosity. For any given rate of frying, the rate of fat turnover will increase as the viscosity increases, and the fat is thus protected by this effect. Addition of fresh fat to used fat in good condition maintains the ability of the fat to contribute desirable sensory attributes to fried foods. A rapid turnover rate is important to minimize thermal deterioration of fats and to maintain the quality of fried foods (Frankel, 2005).

1.4.2 Frying time and temperature

Frying time increases the contents of free fatty acids, polar compounds such as triacylglycerol dimers and oxidized triacylglycerols, dimers and polymers (Choe & Min, 2007).
Depending on the foods, for satisfactory results, frying temperatures range from 160 to 190°C. Continuous evolution of steam from the food is essential to minimize the penetration of oil into the surface of the food. During frying, fat deterioration is delayed by the removal of volatile decomposition products by the stripping action of the steam. Fats decompose rapidly if they are held at frying temperatures without foods. This deterioration can be delayed by reducing the temperature of the fat when it is not used for frying.
Discontinuous frying leads to a faster deterioration since during cooling the oxygen solubility in the oil increases (Choe & Min, 2007).

1.4.3 Quality of frying oil

Stevenson et al., (1984) reported that the oxidation rate of oil increased as the content of unsaturated fatty acids of frying oil increased.
For prolonged frying, in order to minimize both the formation of rancid or "fish" flavors and the formation of cyclic monomers, it is necessary to maintain the linolenic acid content below 2-3%. The soybean and canola oils, which have a high content of polyunsaturated fatty acids, are usually subjected to partial hydrogenation, just to reduce the linolenic acid content. Hydrogenation is the treatment of polyunsaturated vegetable oils with hydrogen gas in the presence of nickel as a catalyst, which leads to the reduction of the linoleic and linolenic acids in a mixture of fatty acids isomers (cis-trans) with two or a double bond. Today the food industry is trying to eliminate from the food trans isomer, because they are responsible for negative effects against the human organism.
Besides hydrogenation, another method to obtain more stable oil is the genetic modification. In recent years new genetically modified varieties of seeds (soya, sunflower, canola, corn) with high or medium oleic acid content, have been developed because they are particularly suitable for frying due to their low linolenic acid content (<3%).

1.4.4 Composition of food

Moisture in foods creates a steam blanket over the fryer and reduces contact with air and acts as a physical agent for the distillation of volatile products formed by oil oxidation, facilitating the removal and thereby delaying the bath oil oxidation (Dana et al., 2003). The more the moisture content of food, the higher the hydrolysis of oils and the higher the free fatty acids that are more susceptible to oxidation.
In addition food contain minor compounds leaching into the frying oil may easily modify oil performance and quality. Among the main compounds contributing to modifying physical or chemical properties of used frying fats and oil the following groups stand out:

- amphiphilic compounds like phospholipids and emulsifiers can contribute to early foaming,
- lipid-soluble vitamins and trace metals leaching into the frying oil inhibit or accelerate oil oxidation depending on their antioxidant or prooxidant effect,
- pigments and Maillard browning products modify the susceptibility against oxidation of frying oil and contribute to darkening,
- phenolic compounds present in the foods or in added spices increase the frying oil stability.

Finally, apart from migration of lipids from the food into the frying oil, it is important to take into account that foods which are breaded or battered may contribute particles of the surface coating to the fat, resulting in burning and off-flavors and increasing fat or oil degradation (Dobarganes et al., 2000).

1.4.5 Filtering

Daily filtration of frying fat to remove accumulated food particles, charred batter and breading is important to reduce deterioration, excessive color formation and development of undesirable bitter flavors and odors. Systems used for filtration include metal screens, paper filters and plastic cloths. The use of diatomaceous earth or filter aid is effective in reducing free fatty acids and color compounds (Frankel, 2005).

1.4.6 Antioxidants

The antioxidants inhibit or retard lipid oxidation by interfering with either chain propagation or initiation by hydrogen-atom transfer and readily donating hydrogen atoms to lipid alkyl, alkoxyl and peroxy radicals.
Oils and shortenings can be added with synthetic antioxidants such as BHA (butylated hydroxyanisole), BHT (butylated hydroxytoluene), PG (propyl gallate) and TBHQ (*tert*-butylhydroquinone). These antioxidants slow down the oxidation of oil at room temperature, and they become less effective at frying temperature due to losses through volatilization or decomposition.
The effect of natural tocopherols and of added tocopherols to frying fats is controversial. Natural occurring tocopherols in vegetable oils are generally not effective as antioxidants at high temperatures, and may even have prooxidant activity at high concentrations. Tocopherols are lost during frying in varying degrees depending on the fats without apparently affecting the deterioration rate of the oils; it was reported that the decomposition of tocopherols in palm oil, after 8h frying at 150°C, was 100%. (Choe & Lee, 1998).
The oils can be added with natural antioxidants. The most used is an extract rich in tocopherols (E 306), which is often associated with α tocopherols (E 307), γ (E 308) and δ (E 309), ascorbic acid and palmitic acid.
Other researches demonstrated that Rosemary, sage and thyme extracts provide an important source of natural antioxidants used commercially in foods. They protect the oils during frying and their antioxidant activity is carried over into the fried foods. The active components of Rosemary, carnosic acid and carnosol, are readily decomposed during thermal oxidation into products that remain active as antioxidants in heated fats.
The carotenoids did not protect the oil by thermal oxidation in the absence of tocotrienols. In fact, although carotenoids are the main compounds that react with lipid radicals in palm olein, when they become radicals, they in turn must be regenerated to carotenes by tocotrienols. Carotenoids and tocotrienols show synergistic effects.
Silicones are very effective additives for retarding thermal oxidation and deterioration by polymerization in frying fats. Silicones are only effective at frying temperatures and at very low concentration (0,5-5 ppm). The use of mixtures of antioxidants with silicones shows synergistic effects in improving the shelf-life of fried foods, for example mixtures of BHA, dimethyl silicone and ascorbyl palmitate were used. The effectiveness of these mixtures may be explained by the stabilizing effect of silicone in retarding the depletion of phenolic antioxidants during frying. As antifoaming agents, silicones form a monomolecular protective film at the air-oil interface that acts as an oxygen barrier. Silicones cannot be used indiscriminately. They have disadvantages by causing failure in cake baking, poor performance in doughnut frying by defoaming the batter, and loss of desirable crispness in fried potato chips.

1.5 Methods to assess frying deterioration

Several methods are used to determine compounds from thermal oxidation that cause significant changes in the physical, chemical and nutritional properties of frying fats. Gross changes resulting from frying include:

- increase in viscosity and density,
- dark color development,
- tendency to foam,
- decrease in smoke point.

The smoke point generally refers to the temperature at which a cooking fat or oil begins to break down to glycerol and free fatty acids, and produce bluish smoke. The glycerol is then further broken down to acrolein which is a component of the smoke. The smoke point of oils depends primarily on their free fatty acid content, molecular weight and water content.
A number of routine methods have been used to evaluate the extent of oxidative and thermal damage to frying fats. These methods can be divided into those that can be used later on oil samples collected some time after frying, those employed immediately after frying for quality control, and those applied to fried foods. The post-frying methods allow determining the degrees of alteration caused by frying foods, commonly estimated by determination of total polar materials by simple column chromatography, polymers by gel-permeation chromatography, and petroleum ether insoluble oxidized fatty acids. The amounts of free fatty acids produced during frying are generally too small to use as a basis to monitor the quality of food.
The levels of polar and polymer compounds are now generally used as indications for rejection of used frying fats. The official method (Standard IUPAC Method 2.507) is time consuming and require too much solvent, for this reason, various rapid micromethods have been developed using disposable silica cartridges to shorten the

analysis time and reduce the cost. Different countries have established different guidelines for frying deterioration or rejection points (also referred to as maximum allowable or "cut-off" level), above which thermally abused fats should be discarded. Frying fats are recognized as objectionable and to be rejected if the level of polar materials exceeds 25-30% (most of Europe).
The different types of frying, however, produce different amounts of total polar compounds. Dobarganes & Marquez-Ruiz (1998) determined the TPC values of a large number of used oil samples belonging to the three main frying segments: the domestic frying (10.5 to 42.1% of TPC), chip shops and restaurants (3.1 to 61.4% of TPC), industrial frying (4.2-27,3% of TPC). In general, the frying industry employs continuous fryers (200-800 L), while the restaurants and fast foods use discontinuous fryers (2-50 L). Samples from the latter segment showed higher values of TPC and variables in a fairly wide range, because of the oil heating and cooling cycles, where the oil is kept warm but without the presence of food and with low fat turnover. The rapid methods are needed for fast food operators because, although the determination of total polar compounds is accepted worldwide as the best method to assess the quality of the oils used in frying, can be implemented only at internal laboratories, and requires skilled personnel. In the case of a discontinuous frying, the more rapid used methods are based on the variation of physical characteristics of the oils, and the reliability of the result depends strongly on the operator. These are methods to evaluate changes in color, foaming, smoke fumes, smell and oil fry-life (Stevenson et al., 1984). For this reason a series of rapid tests have been developed and marketed for assessing the quality of oils such as Food Oil Sensor (FOS, which measures the changes in dielectric constant); OXIFRIT-TEST (colorimetric test containing redox indicators which react with all the oxidized compounds formed); FRITEST (sensitive to carbonyl compounds); VERY-FRY (contains redox indicators that change color from blue to green with increasing TPC) (Dobarganes & Marquez-Ruiz, 1998).
To establish more reliable quality criteria for consumer acceptability, the fried foods must be tested rather than the frying fats. More sensitive and reliable measures of frying performance of fats are based on sensory evaluations and gas-chromatographic analyses of volatiles in fried foods carried out initially and after storage. As expected, gas chromatographic analyses showed decreases in volatile formation with decreasing content of linoleate. In fact this fatty acid produce 2,4-decadienal, a decomposition product of oxidized linoleate that contribute to higher flavor quality and fried flavor scores, but this aldehyde at high levels also contributes to rancìdity. The relative concentrations of 2,4-decadienal necessary to optimize a desirable fried food flavor, without also producing rancidity are not known and are difficult to predict and control (Frankel, 2005).

1.6 Regulation of used frying fats

One of the main difficulties in quality control during frying is to determine when the oil is so deteriorated that it must be removed and replaced. Many countries have adopted specific guidelines to establish the deterioration of frying oil. Present regulations have their origin in the recommendations given by the German Society for Fat Research (DGF) to limit the alteration of frying fats for human consumption by a measure of oxidized fatty acids. Then the development of polar compounds determination, later proposed by IUPAC, for the control of frying fat quality was an undoubted analytical improvement which contributed to the emergence of the present regulations. The two main positive characteristics of this evaluation are:

- It is an objective method clearly related to the quality of the fat. Thus, the higher the level of polar compounds, the lower the quality.
- It is simple, accurate and reproducible.

Given that the amount of polar compounds was found to be very well correlated to the content of oxidized fatty acids, in a new symposium of the DGF in 1979, polar compounds determination was recommended as a new criteria. Since then, determination of polar compounds has become the method most generally accepted for quality evaluation of frying fats. In general, in all European countries, the polar compounds percentage varies between 25% and 30%, which corresponds to 13-15% of polymerized triglycerides, and to a 0.7% oxidized fatty acids insoluble in ether oil.

1.7 Health effects of frying fats

Although frying is considered an inexpensive, fast and efficient method for cooking, and food surface sterilization, fried foods in the Western diet are perceived negatively. However, it is not *a priori* that the nutritional value of fried foods is inferior. Deep fat frying has significant advantages over other cooking methods: the temperature within the product (aside from the crust region) is below 100°C; short frying time; and insolubility of water-soluble vitamins (Saguy & Dana, 2003). Retaining lipid-soluble vitamins is more complex. As all vegetable oils used for frying contain vitamin E at a concentration between 15 and 49mg α-tocopherol equivalents/100g, fried foods due to oil uptake are enriched with considerable amounts of the vitamin. For instance, a portion of 100g homemade French fries provides up to 50% of the RDA of vitamin E.
Despite the positive nutritional effects, it must be remembered that during the frying process, the oil undergoes strong chemical and physical changes. The oils that are subjected to strong thermal stress may degrade,

synthesizing molecules that affect not only the shelf life and organoleptic characteristics of the food matrix, but also the consumer health. These newly-synthesized molecules, can have toxic effects.
Trans fatty acids (TFA) concentration in frying oils could be significant due to the partial oil hydrogenation required for improving stability. Generally, soybean and canola oils, which are the two most oils used in the snack food, are subjected to a mild hydrogenation process to reduce the linolenic acid content, and therefore increase the stability oxidation.
Repeat use of frying oils may increase TFA concentration due to the exchange of fatty acids between the fried food and the oil as well as the high temperature and prolonged frying process (Saguy & Dana, 2003).
The TFA average daily consumption is extremely difficult to determine because the diet includes a mix of foods that may vary depending on each person. A typical Western diet contains 100g of fat with a concentration of ~ 10% TFA.
TFA reported negative effects on serum lipoproteins and increased risk of heart disease.
In fact, recent studies suggest a negative role of trans fatty acids in the atherogenic process (Troisi et al., 1992).
In Italy the SINU (Italian Society of Human Nutrition), recommend not to exceed 5g/die of trans fatty acids.
The tendency to reduce TFA concentration in margarine and edible oils was born in Europe and is spreading in U.S. Since 2006, the FDA requires companies to report trans fatty acid content on product's label. For this reason new oilseed variety were developed by genetic engineering. These varieties are more stable oils, known as "zero trans", as it does not require hydrogenation. Several studies indicate that products generated through oil oxidation can be carcinogenic. A great number of studies have been conducted over the last sixty years to see if the molecules synthesized during the frying process can have mutagenic and carcinogenic effects. However, most studies have been conducted in vitro or on laboratory animals (mostly mice) and therefore little is known about the effects these have really on the human molecules. Fatty acid cyclic monomers and some non-volatile aldehydic groups that are synthesized from triacylglycerols during frying are considered toxic.
The trans, trans-2,4-decadienal is synthesized from arachidonic and linoleic acids peroxidation (Billek, 2000, Esterbauer et al., 1990) and was found in the fumes generated during heating of rapeseed, soybean and peanut oils. This molecule is considered the most responsible for the cytotoxic and mutagenic effects of the fumes generated during frying (Zhu et al., 2001). Another molecule found in the fumes is the malondialdehyde (MDA), considered to be mutagenic in many studies.
MDA was found to cause skin cancer in rats and created cross-linking with amino-groups of DNA solution. Rats fed a diet containing MDA suffered from retarded growth, irregular intestinal activities, enlarged liver and kidneys, anaemia and low serum and liver vitamin E (Saguy & Dana, 2003).
Many precursors of malonaldehyde have been suggested including monocyclic endoperoxides and bicyclic endoperoxides, which are produced as secondary products in polyunsaturated lipids containing three or more double bonds. The TBA test (thiobarbituric acid test) is a colorimetric method used to measure MDA. This test is based on the pink color absorbance at 532-535 nm formed between TBA and MDA.
In addition, during frying, acrylamide is formed. It' s one of the volatile compounds synthesized during the oil degradation. An expert consultation on the implications of acrylamide in food, hosted by the World Health Organization (WHO) and United Nations Food and Agriculture Organization (FAO) in June 2002, stressed the need to establish a network for research on acrylamide to achieve a better understanding of human exposure and its possible health effects. Acrylamide is formed by oxidation of acrolein to acrylic acid with reacts with ammonium coming from nitrogen containing compounds like amino acids (asparagines, glutamine). It is also assumed that the precursors, acrolein, is formed by elimination of water after heating glycerol. Acrylamide is suspected to be genotoxic, carcinogen and produce peripheral neuropathy. (Gertz & Klostermann, 2002).
Recent findings have confirmed that asparagine, a major amino acid in potatoes, rice and cereals, is a central factor for acrylamide formation, especially in the presence of reducing sugars (Mottram et al., 2002). Other factors may include temperature, product moisture and pH.
The French fries are one of the foods most incriminated for the formation of this substance, as they have a relatively high content of free fatty acids and are rich in carbohydrates. Surprisingly, the formation of acrylamide in food was much higher when using palm olein or frying oils containing silicone. This may be due the presence of 6 to 8% of diacylglycerols in palm oil products, which possibly enhance the rate of reaction of acrylamide formation by emulsification of the components. (Gertz & Klostermann, 2002).

1.8 Recommendations for good flavor and good stability in frying oils/fried food

The amount and type of degradation products formed in frying oils is primarily dependent on the fatty acid composition of the frying oil, so it is important to keep this in mind in selecting frying oils. Even though linolenic acid is a healthful fatty acid, it is also very oxidizable, as previously discussed. Therefore, reducing linolenic acid to < 3% is necessary for good oil stability and for limiting development of off-flavor. In addition, linoleic acid should be present in the oil in greater amounts than the linolenic acid to not only provide for good deep-fried flavor, but also to help mask off-flavors from the linolenic acid degradation. Even though linoleic acid

oxidizes in the fryer, some is needed for developing a deep-fried flavor. Therefore, linoleic acid should be in the 20–30% range (Warner et al., 1997). The precise level can be adjusted to meet the fry life requirements of the oil and the shelf-life needed for any stored fried food. In general, most of the modified composition oils have the following characteristics. Low linolenic acid containing oils give only moderate frying stability, but they have high deep-fried flavor intensity because the linoleic acid content can still be high at 50–55% as in soybean oil. High oleic oils give good frying stability and high waxy/plastic flavor intensity from oleic acid decomposition, but they are low in linoleic acid, so they have low deep-fried flavor intensity. Finally, mid-oleic oils have 50–70% oleic acid for high frying stability and 20–30% linoleic acid for high deep-fried flavor intensity. It is possible to get good deep-fried flavor and good stability in frying oils and fried foods.

In deep-frying, choice of the frying medium is also of great concern for various reasons.

In this work five different oils were used to evaluate their behavior during the thermal process. The oils used were: bi-fractionated palm oil, olive oil, sunflower oil, lard and oil mixture.

Palm oil and its products, palm olein, double-fractionated palm olein, palm stearin and red palm oil, are widely used in industrial frying. One reason is that these oils are available in huge amounts and result in a pleasant room odour during frying. Additionally, the different products show good frying properties with a high resistance to oxidation, which results in a long shelf life.

The most popular commercial frying oil is palm olein, which is produced from palm oil by fractionation. As a result of this process, high-melting triacylglycerols are removed and lower-melting compounds are enriched, which leads to a higher amount of unsaturated and a lower amount of saturated fatty acids in palm olein in comparison to palm oil. Thus, palm olein has a lower melting point (22–24 °C), resulting in no waxy or greasy mouth-feeling of the products fried in this oil.

Olive oil is a product rather closer to the Mediterranean diet, although this is a product of lower value than the virgin oils obtained by mechanical processes only; it is obtained from a mixture of rectified olive oil and virgin olive oil. Recently, the consumption of olive oil is increasing, particularly for use in frying (Casal et al., 2010). Several studies have demonstrated increased oxidative stability of oils with high oleic acid content, compared to oils rich in polyunsaturated fatty acids (Pantzaris, 1998).

Traditional sunflower seed oil, obtained in 40 to 50% yield by solvent extraction, is a linoleic rich oil with virtually no linolenic acid. It also contains oleic acid (~20%), palmitic acid (~6%), and stearic acid (~5%). It is widely used as a cooking oil and is valued as an important component of soft spreads, particularly in Europe.

In the past, lard and other animal fats had been used as frying medium for a number of food products (Weiss, 1983). However, the high content of saturated fatty acids and low proportion of polyunsaturated fatty acids in animal fats has prompted a shift away from the use of animal fats as a frying medium (Love, 1996). In addition, cholesterol present in animal fats is perceived to be bad by the public because of the historical view that eating cholesterol was a major risk factor for coronary heart disease (CHD) (Enser, 1995). As a result, there is a continued preference towards vegetable-based shortening for frying. Reports of the unfavorable health implications and strict religious proscriptions of lard have prompted many countries to look for lard detection methods for regulatory purposes (Rashood et al., 1996).

1.9 References

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AIMS OF THE STUDY

2. AIMS OF THE STUDY

The frying of foods is an important application of edible fats. It is one of the most complex and difficult processes to understand, because of the multitude of reactions taking place and the complexity of the products formed.

Frying oils are both a heat transfer way and an ingredient of the finished product, they can represent up to 40% of the total weight of products such as chips. The best choice of oil for frying is of crucial importance, not only for its potential nutritional value but also for its ability to withstand the drastic conditions of this cooking technique, so it is necessary to find a compromise between thermal stability, nutritional value and cost (Ziaiifar et al., 2008).

Generally, the frying performance and stability of oils are greatly dependent on the amounts of total oxidizable polyunsaturated fatty acids (Frankel, 1998).

The level of 25% total polar materials is now recognized in Europe (law n.11 of the 11 January 1991) as an important, but overall unique, rejection point in assessing frying oil quality.

The aim of this study was to evaluate and compare the effects of discontinuous and prolonged heat treatment (typical of fast food and restaurants) on five oils with different unsaturated/saturated fatty acids ratio (UFA/SFA). This experimentation was carried out by measure of several analytical procedures in order to give information about thermal oxidation stability of oil both during the simple thermo-oxidation and during frying process. An other aim of this study was to demonstrate that a single marker cannot be used interchangeably for all frying fats. So, new markers were proposed. The parameters chosen were: free fatty acid (FFA), peroxide value (PV), total polar compounds (TPC) and fatty acid (FA) profile.

In addition the detection of volatile organic compounds (VOC) was proposed in order to evaluate the thermo-oxidation degree of oils subjected to discontinuous thermal treatment. The VOC analysis was carried out by dynamic head space (DHS) technique coupled with gas-chromatography (GC) analysis and mass spectrometer (MS) to identify them.

2.1 References

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RESULTS AND DISCUSSION

3. RESULTS AND DISCUSSION

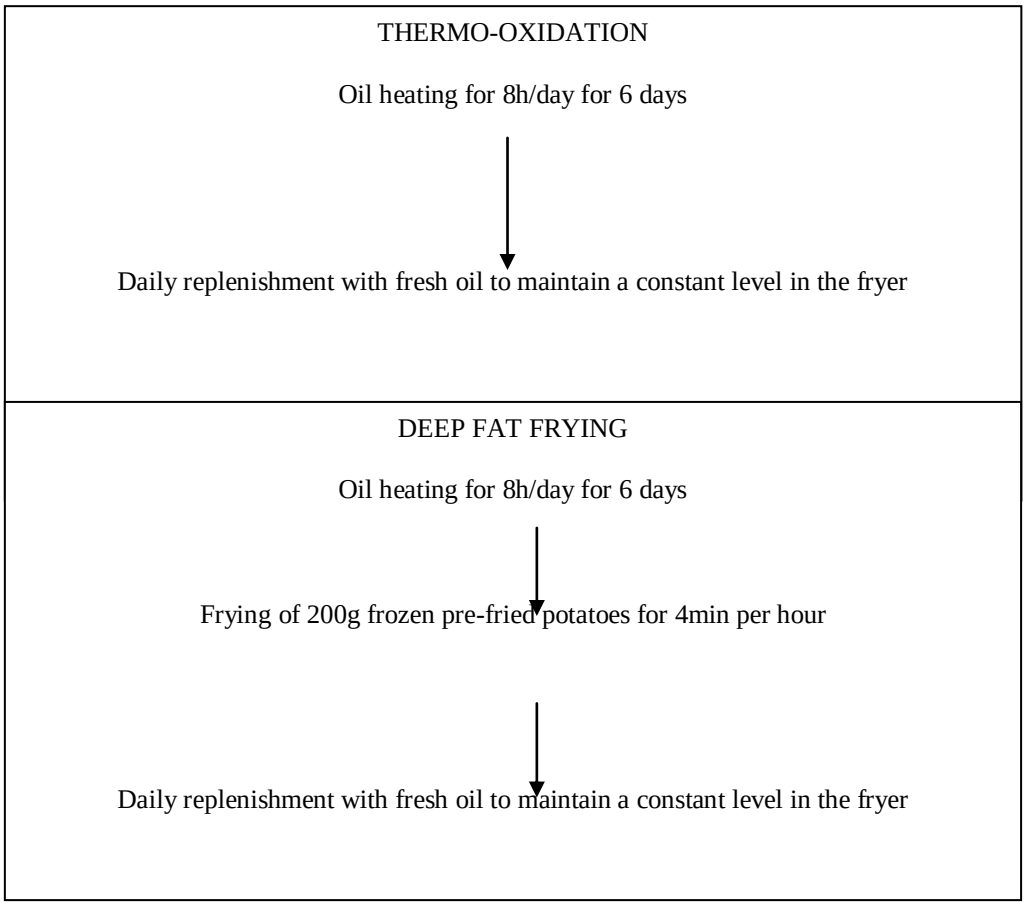
The experimentation was carried out by a prolonged and discontinuous deep-fat frying process with frozen pre-fried potatoes (McCain) and by a simple thermo-oxidation process of oil without food matrix. Both thermal treatments were conducted over a period of 8h per day for 6 days. The thermal process was conducted in a thermostatically temperature controlled fryer (Tefal, Milan Italy) at approximately 180°C±5°C. Every 25min, 200 g of frozen pre-fried potatoes were deep fried for 4min (based on a preliminary trials), for a total of 8h per day. The batch volume of deep fat fryer was 3L. Fresh oil was added every 8h after oil samples were collected, to maintain a constant level in the fryer. The frying oil used to fry frozen potatoes, oil extracted from French fries and oil heated in the fryer without potatoes were sampled every 8h. The oil samples (30mL) were stored at a temperature of -20±2°C until the analysis.

The oils used were:

- Palm super olein (bi-fractionated palm oil): UFA/SFA = 1.41
- Olive oil: UFA/SFA = 6.05
- Sunflower oil: UFA/SFA = 10.32
- Lard: UFA/SFA = 1.52
- Mix oil: UFA/SFA = 10.77

All oils were purchased from a local market in Naples. All reagents were of analytical or spectroscopic grade and were supplied by Sigma Aldrich (St Louis MO).

3.1 Experimental draw



After frying process, the French fries were subjected to fat extraction.

3.2 Treatment conditions

Food matrix: frozen pre-fried potatoes McCain (200g/h).
Oil volume: 3 L
Treatment temperature: 190°C before to add frozen potatoes; then temperature decreases until to 165°C during frying.
Treatment time: Both thermal treatments were conducted over a period of 8h per day for 6 days for a total 48h
Replenishment: Fresh oil was added every 8h after oil samples were collected, to maintain a constant level in the fryer.

3.3 Sampling

Three sample series were collected:
thermo-oxidized oil samples
frying oil samples
fat samples extracted from French fries
After 8h of thermal treatment the first samples were collected and then every 8h. The French fries samples were collected with the same frequency. So, the samples analyzed correspond to following treatment hours:
8, 16, 24, 32, 40, 48 and the oil and French fries samples of time "0".
The samples were stored at a temperature of -20±2°C, labeled and preserved until the analysis.

3.4 Analytical determinations

All samples were subjected to the following determinations:

- FFA (free fatty acids) determination;
- PV (peroxide value) determination;
- TPC (total polar compounds) determination;
- FA (fatty acid) composition determination (high-resolution gas-chromatographic (HRGC) analysis of fatty acid methyl esters (FAME));
- VOC (volatile organic compounds) analysis by DHS (dynamic head-space system)/HRGC-MS (mass spectrometer).

3.5 Fat extraction from French fries

As a side-effect of the frying process a lot of oil is taken up by the food, resulting in a partially high amounts of oil in fried foods. The oil becomes a significant part of the food, influencing the quality of the product. The most drastic increase is found in potato crisps, in which the amount of fat during frying increases from 0.1% in raw potatoes up to about 40% in the fried potato crisps (Matthaus, 2007).
Oil absorption depends on the frying oil quality more than on the oil or fat used for frying. The amount of fat absorbed by the French fries depended on the kind of oil used for frying and on the frying temperature. In particular Kita & Lisinska, (2005) have demonstrated that the lower the temperature, the higher is the fat content of the product.

3.5.1 Method principle

The method described by Soxhlet is a gravimetric method, namely a method for determining the mass of the analyte. According to the Soxhlet procedure, oils and fats are extracted from solid samples by repeated washing (leaching) with an organic solvent, in a special glass.
The procedures of lipid extraction from French fries, in this study, include several steps: (a) size reduction of the sample; (b) homogenization of the tissue in the presence of a solvent; (c) separation of liquid (organic and aqueous) and solid phases; and (e) removal of solvent and drying of the extract.
The extraction efficiency of lipids from a sample also depends on the size of the particles. Therefore, particle size reduction increases surface area, allowing more intimate contact of the solvent, and enhances lipid extraction. For this reason, the French fries are appropriately milled before being subjected to solvent extraction.
The most important characteristic of the ideal solvent for lipid extraction is the high solubility of lipids coupled with low or no solubility of proteins, amino acids, and carbohydrates. The extracting solvent may also prevent enzymatic hydrolysis of lipids, thus ensuring the absence of side reactions. The solvent should readily penetrate sample particles and should have a relatively low boiling point to evaporate readily without leaving any residues when recovering lipids.
Diethyl ether and petroleum ether are the most commonly used solvents for extraction of lipids, in this study a mix (1:2 v/v diethyl ether/petroleum ether) was used.

In the semicontinuous solvent extraction (Soxtec), the solvent accumulates in the extraction chamber (sample is held in a filter paper thimble) for 5–10 minutes and then siphons back to the boiling flasks. After a certain period of time the solvent layer is recovered, and the dissolved fat is isolated by evaporating the organic solvent.

3.5.2 Equipment

The extraction of oil from the potatoes was carried out using an apparatus Büchi Universal Extraction System B-811. This is an automated system that follows the principle of Soxhlet extraction.
The apparatus is characterized by four automatic extraction units that can work simultaneously and quickly, allowing a significant reduction in extraction time.
Once thawed potatoes were finely chopped and placed in the appropriate cellulose thimbles (10 grams per thimble). The thimbles were placed in special housing within the extraction units and the corresponding glasses were filled with the mixture diethyl ether:petroleum ether (1:2 v/v).
The extraction is divided into three phases:
• Extraction: it can choose from four different extraction methods. At this stage the solvent in the glass is heated from the bottom plate, evaporates, condenses and is collected in the extraction chamber. Here in contact with the sample occurs extraction of fats present in it.
• Rinsing: the valve that separates the extraction chamber and glass is open. This step ensures the complete recovery of the extract and the washing of the extraction chamber.
• Drying: the valve is closed. The bottom plate is heated, the solvent evaporates from the glass and is collected in the extraction chamber empty. The concentrated extract is got.

3.6 FFA determination (Reg. CE 1989/03)

3.6.1 Method principle

The acidity value indicates the quantity in grams of free fatty acids, expressed as oleic acid, present in 100 g of oil.
This determination is used to evaluate the quality of vegetable oils; a sample with a high value of this index has certainly undergone a process of degradation of triacylglycerols (especially type enzyme), because of poor preservation, of the normal aging or blending with lower quality oils.
The determination was performed in triplicate for each sample.
The maximum allowed for a seed oil is 0.5% (oleic acid) and seed oils generally have such low values (0.1-0.2% on average) as the technological processes that are undergo determine the removal of free fatty acids.

3.6.2 Execution

Briefly describing the assay: in an Erlenmeyer about 5 g (accurately weighed) of well mixed and entirely liquid oil sample is added to 80 mL of ethanol/diethyl ether (1:2) mix and 1 mL of 1% phenolphthalein solution, prepared in neutralized 95% ethanol. The resulting emulsion is shaken vigorously and then subjected to titration with standardized 0.10 mol/L sodium hydroxide solution until appearance of the first permanent pink colour.
The acidity was obtained by the following formula:

% oleic acid = (V*N*282*100)/p*1000 = (V*N*28,2)/p

where:
V = mL NaOH used
N = base normality
p = sample weight (grams)
282 = equivalent weight of oleic acid

3.7 Results FFA

The FFA values, expressed as g/100g oleic acid, for all oils tested are given in **Tab. 3.2.**
It can be seen that the FFA values increased with increasing heat treatment times for all oils.
In particular, for all frying oils tested the FFA values were higher in the frying samples than in thermo-oxidized samples. The highest level of FFAs in the frying oil is due to the release of water from the food matrix immersed in the oil bath. The pre-fried potatoes used in this experiment contain a high concentration of frozen water, which contributes to the increased hydrolysis of triglycerides and, thus, to a higher acidity level (Frankel, 2005). This result is possible because during frying, there is an exchange between the fats in food and bath oil, and more than 90% of the lipid content in the resulting food comes from the bath oil (Dobarganes et al., 2000). The FFA content of the fat extracted from French fries was higher than the FFA percentage of the thermo-oxidized samples, with the exception of olive oil that showed more or less the same value (1.17 g/100g for thermo-oxidized olive oil and 1.13 g/100g for olive oil extracted from French fries). About thermo-oxidation process, lard showed the lowest FFA values, followed by sunflower oil, while the olive oil showed the highest values. During frying process, the five oils showed similar FFA trend. The exception is the olive oil which, passing from 40^{th} to 48^{th} hour of heat treatment, undergoes a rapid FFA increase, reaching values higher than those from other oils. The frying sunflower oil showed, at the end of treatment, the lowest acidity value. About fats extracted from French fries, the olive oil is the one that showed the best results, followed by mix and sunflower oils. In conclusion, considering the trend recorded in the three samples series (thermo-oxidized, frying and extracted from French fries), based on the acidity values, the best frying fat showed to be the sunflower oil.

3.8 Conclusion FFA

It was observed that the FFA values (g/100 g oleic acid) obtained for these oils grow with the progress of heat treatment, indicating an increase in the incidence of hydrolysis.
During thermo-oxidation lard proved to be the most stable, about acidity. During frying it is the best and the sunflower oil showed to be the best both for frying samples and for fats extracted from French fries.

3.9 PV determination (Reg. CE 1989/03)

3.9.1 Method principle

The peroxide value serves as an indicator of oil quality. Although it does not distinguish between the various unsaturated fatty acids that undergo oxidation and does not supply information about the secondary oxidative products formed by hydroperoxide decomposition, generally it can be stated that the peroxide value is an indicator of the primary level of oil oxidation. The change in peroxide values versus time exhibits an induction stage, where a steep increase in peroxide value occurs, and a decrease as lipid oxidation proceeds. Hydroperoxides break down at a faster rate than their formation. Low-quality oil will have shorter induction periods (Sheabar & Neeman, 1988). Peroxides are unstable under frying conditions. An increase in the peroxide value during the initial stage of frying would be expected to be followed by a decrease with further frying because the hydroperoxides tend to decompose at 180°C to form secondary oxidation products (Chatzilazarou et al., 2006; Perkins, 1967; Tsaknis et al., 1998). Further frying results in another increase in peroxide value. The overall increase in peroxide value occurs particularly during the cooling period, where the frying oil is exposed to air at high temperature (Augustin & Berry, 1983). Peroxide and hydroperoxides, although flavorless, provide an indication of impending flavor deterioration (Gray, 1978). The peroxide measures the formation of intermediate hydroperoxides in milliequivalents of active oxygen per kilogram of sample. The peroxide value was determined by standard procedure by a mixture of oil and chloroform/acetic acid which was left to react with a solution of potassium iodide in darkness. The liberated iodine is titrated with standard sodium thiosulfate $Na_2O_3S_2 \cdot 5H_2O$ to a starch endpoint. In seeds oils the peroxide value must be equal to or less than 5%.

3.9.2 Execution

In an Erlenmeyer weigh about 5 g of oil, add 25 mL of a mixture of acetic acid-chloroform (3:2); acetic acid causes a pH value needed to create the right conditions of reaction. Add 0.5 mL of a saturated solution of KI. Shake and leave for 5 minutes in the dark, the latter precaution is necessary because the light could affect the amount of iodine that is released and therefore distorting the results of the determination. Hydroperoxides in the presence of KI, are reduced according to the following redox reaction:

$$ROOH + 2H^+ + 2e^- \quad ROH + H_2O$$
$$2I^- \quad I_2 + 2e^-$$
$$ROOH + 2H + 2I^- \quad ROH + I_2 + H_2O$$

Dilute with 75 mL of distilled water and titrate with a solution of 0.01N $Na_2O_3S_2 \cdot 5H_2O$ in the presence of starch paste as indicator, which turns blue in the presence of hydroperoxides. The iodine I_2 that is released from the previous reaction is directly proportional to the amount of hydroperoxides in the sample:

$$2S_2O_3^{--} \quad S_4O_6^{--} + 2e^-$$
$$I_2 + 2e^- \quad 2I^-$$
$$2S_2O_3^{--} + I_2 \quad 2I^- + S_4O_6^{--}$$

The addition of thiosulfate continues until the blue color disappears from the solution, indicating that all the liberated I_2 was titrated. At this point, the PV is derived from the following expression:

$$\mathbf{NP = (N^* V * 1000)/p}$$

where:
V = used mL of $Na_2O_3S_2 \cdot 5H_2O$ solution
N = normality of $Na_2O_3S_2 \cdot 5H_2O$ solution
p = weight of oil (grams)

3.10 Results PV

The PV for oils tested is given in **Tab. 3.3.** The peroxides showed an irregular trend: during both the thermo-oxidation and frying treatments, continuous formation and decomposition of primary products of oxidation occurred in both oils. Hydroperoxides are unstable at high frying temperatures and decompose rapidly in a wide range of volatile (aldehydes, ketones, alcohols, esters, acids) and non-volatile compounds (dimers and polymers, polar and non-polar compounds). Additionally, during frying, the formation of peroxides is inhibited by reduced availability of oxygen because its solubility in oil is reduced at high temperatures and because the water released from food creates a protective cloak of steam. Unfortunately, intermittent heat treatment is more destructive compared with continuous treatment because new peroxides form during cooling, and in the subsequent heating phase, these hydroperoxides undergo hydrolysis (Frankel, 2005).

In general, the PV in palm superolein and in mix oil was always lower than in other three oils. This difference can be explained considering the different fatty acid compositions of oils: palm superolein and mix oil exhibit a fatty acids profile less susceptible to free radical chain reactions leading to the formation of hydroperoxides.

Based on fatty acid composition of lard, being more rich in saturated fatty acids should be more stable in terms of PV. In fact at time 0 lard, compared with other oils, has the lowest PV; however, already starting from 8th hour we see a sharp increase of this parameter. So, beyond the profile acidic, are many and complex mechanisms that occur during heat treatment and contribute to the formation of hydroperoxides. Higher values of the PV were detected for fat extracted from potatoes fried in sunflower oil and in the mix oil.

The sunflower oil was found to be the best in the case of frying and in the case of extraction from potatoes; lard was showed to have lower values.

Although the peroxide value is a parameter of legislation for both bottled olive oil for vegetable oils, being composed of transient, rather unstable, are not always well correlated with the actual oxidation of samples, especially at high temperatures (Casal et al., 2010).

3.11 Conclusion PV

The peroxides are synthetized by synergic action of several factors: oxygen presence, unsaturation degree of oil, metals and frying temperatures. The PV of oil is an empirical measure of oxidation that is useful for samples that are oxidized to relatively low levels, and under conditions sufficiently mild so that hydroperoxides are not markedly decomposed. During auto-oxidation, the PV of oil reaches a maximum followed by a decrease at more

advanced stages varying according to the fatty acid composition of the oil and the conditions of oxidation. The PV of oils oxidized under accelerated conditions (180°C for 8h) are misleading and erroneously low especially for polyunsaturated oils because of significant decomposition of hydroperoxides. So, a large variability in PV values was estimated during this experimentation, probably due to continuous cycles of synthesis and decomposition of hydroperoxides. In fact, the fresh oil, daily added to the frying bath, undergoes oxidation producing new hydroperoxides.

3.12 TPC determination

The total polar compounds (TPC) together with the polymerized triglycerides (PTG) are the most important parameters, which are used in different countries to tell if a frying oil can be further used or must be eliminated, but unfortunately there are still few nations that have established formal regulations for the control of frying fats. This analysis is indicated by the IUPAC (International Union of Pure and Applied Chemists) as the official analysis of the frying fat.
Total polar compounds were performed according to Dobarganes et al., 2000 modified by use of pre-packed column.

3.12.1 Method principle

The method consists of a selective absorption of polar and non polar lipids on a silica gel column, followed by the elution of non-polar and polar fractions with suitable solvents. Then both fractions can be quantified gravimetrically.
By definition, the polar compounds are those compounds in fat, separated by column chromatography, under specific conditions. These include molecules such as monoglycerides, diglycerides, and free fatty acids that are present also in oils not used; but also polar products that are formed during frying of food or during simple heating oils, such as triacylglycerols, oxidized and polymerized triacylglycerols. The non-polar compounds are mainly triacylglycerols.

3.12.2 Execution

- Weigh 1g (± 0.1 g) of sample. Add 8 mL of the mixture petroleum ether/diethyl ether (90/10). Shake and make up a flask of 10 mL. Set the pre-packed column (Discovery 21 mm, length 450 mm)∅DSC-Si SPE Silica Tube 20 mL, 5g) with approximately 20 mL of elution solvent (mixture petroleum ether(90) / diethyl ether (10)). Drain off the supernatant solvent until the level of solvent in the column is about 10 mm above the gel SiO_2.
- Introduce with a volumetric pipette 5 mL of the sample onto the column. Dry two 100-mL beakers in the oven at a temperature of 103°C. Allow to cool to room temperature and weight accurately to within 0.001 g. Place one of them under the outlet of the column.
- Elute non polar fraction (fraction 1) with 60 mL of the elution solvent. Adjust the flow rate to about 1.5 mL/min. After completion of the elution, wash any substance adhering to the outlet of the column with the elution solvent using a pipette. Elute the polar fraction (fraction 2) into a second 100-mL dry flask with 50 mL of the elution solvent 2 (diethyl ether).
- Evaporate the solvent from the flasks under vacuum in a rotary evaporator at 60 °C. Shortly before the end of the distillation, introduce nitrogen into the system. Dry for 1 hour under vacuum. Weigh the flasks.

Fraction 1 represents non polar components (unaltered triacylglycerols). Fraction 2 represents polar components (altered triacylglycerols and natural accompanying polar compounds). The mass fractions of non-polar compounds (*w*np) and the polar compounds (*w*p) are given by the formula

$$w\text{np} = (m\text{np}/m)100\% \quad w\text{p} = (m\text{p}/m)100\%$$

where *m*np is the mass (in g) of the non polar fraction 1, *m*p is the mass (in g) of the polar fraction 2, and *m* is the mass (in g) of the test portion added to the column.

3.13 Results TPC

The obtained TPC values are reported in **Tab. 3.4**.
About bi-fractionated palm oil, this is the only one present already at time 0, an higher TPC value (11.70%). The high initial TPC content in fresh palm superolein could be attributed to the large proportion of DG in this oil (Bansal et al., 2010). Berger (2005) reported that the TPC test was associated with problems in interpreting the quality of oils with high DG content, such as palm oil and palm olein. Typically, 6-8% DG are found in palm oil and palm olein, whereas other oils contain only 2-3% or less. As DG are measured as a fraction of TPC, it may be misleading to use TPC in judging oil quality. As consequence the polymerized triacylglycerols content was used to judge the quality of used oils. The polymerized triacylglycerols could be quantified by high performance size-exclusion chromatography method (HPSEC) of polar fraction (Sebedio et al., 1991).
Despite the high initial value in the bi-fractionated palm oil TPC increased in all three series of samples. In particular, both thermo-oxidized and frying samples exceed the limit of 25% of TPC at the 32th hour while the fat extracted from French fries does not exceed this value, even at 48 hours of treatment.
TPC results suggested the fastest degradation rate in the controlled heating oil samples as compared to the frying ones, according to results of Bansal et al., (2010). This result could be attributed to the protective effect of the water released from the food during frying. The removal of water from food in the form of steam leads to a distillation process associated with removal of oxygen dissolved in the oil, volatile compounds, and probably also free radicals formed during frying (Dana et al., 2003).
TPC increase with the progress of the heat treatment for olive and sunflower oils, for all three sets of samples. The thermo-oxidized samples of both oils showed a rather rapid increase of TPC with a value that exceeded the legal limit at the 32th hour of heating, and at 48 hours reached a value equal to 37.80 % for olive oil and 37.41% for sunflower oil. The values obtained in frying oils and in fat samples extracted from potatoes were lower than that ones obtained for thermo-oxidized samples. This could be attributed to the protective effect of the water released from the food during frying itself. Frying olive oil was just over the legal limit at the 40th hour, after which it showed a slight reduction at 48 hours. The oil extracted from potatoes did not reach the legal limit during the whole heat treatment. Frying sunflower oil did not exceed the legal limit of TPC whereas the oil extracted from potatoes, contrary to the bi-fractionated palm oil and oil extracted from potatoes, exceeded 25% of TPC at 32nd and 40th hour and then decreased at 48 hours.
It has been reported that the formation of TPC during a repeated frying process increases with an increasing degree of unsaturation of the oil itself, as occur for thermo-oxidized sunflower oil. Considering this finding, we would have expected higher TPC values for olive oil than palm superolein; instead, in the samples from both frying oil and the fat extracted from potatoes, olive oil appeared to be associated with a lower TPC content than palm superolein, which is less unsaturated. This result is in agreement with the findings of a previous scientific study (Tabee et al., 2009) and can be explained by considering that olive oil, although rich in monounsaturated fatty acids, is actually very stable with respect to thermal degradation. In addition, the olive oil, a commercial blend of refined with virgin olive oil, contain most important compounds defining its oxidative resistance, namely vitamin E, phenols and mostly the monounsaturated triglycerides (Casal et al., 2010).
About lard, TPC showed an increased trend only for fat extracted from French fries. For the thermo-oxidized lard, an initial increase occurred until 16th hour, decreases at 24th hour and then ri-increases until 48th hour. The same trend was detected for frying lard samples, but the decrease occurred at 40th hour. The mix oil had, in all three sample series, an increasing trend and only the thermo-oxidized samples exceeded the maximum limit at 40 hours.

3.14 Conclusion TPC

On the basis of the quantification of these fractions, the high initial TPC content in fresh palm superolein could be attributed to the large proportion of DG in this oil. Similar results have been reported in the literature. Berger (2005) reported that the TPC test was associated with problems in interpreting the quality of oils with high DG content, such as palm oil and palm olein. Typically, 6-8% DG are found in palm oil and palm olein, whereas other oils contain only 2-3% or less. As DG are measured as a fraction of TPC, it may be misleading to use TPC in judging oil quality.
About TPC determination, adopted by Italian law as only marker to assess the frying oils deterioration, there is an increasing trend for all oils. The comparison between the oils showed that palm oil had a higher TPC content than other oils. This could be attributed to the high initial content of diacylglycerols. In order to better understand the results obtained, it is necessary to study in deep the total polar compounds and in particular to analyze the fractions that compose them in order to verify in which of the five oils, it has actually occurred increased formation of oxidized and polymerized triacylglycerols and free fatty acids. In conclusion, considering

the performance recorded in three samples sets (thermo-oxidized, extracted from potatoes and frying) on the basis of the TPC, the best fat turned out to be fried lard.

3.15 Fatty acid composition determination

Fatty acid composition of oil samples was determined as methyl esters by capillary GC after alkaline treatment of samples. The alkaline treatment was carried out by mixing 0.05 g of oil dissolved in 1 mL of n-hexane with 0.3 mL of 2 N KOH in methanol. After this trans-esterification reaction fatty acids become more volatile and so can be separated by chromatographic analysis. The resulting emulsion is shaken vigorously for a few minutes to promote mixing between the two phases. After a few minutes, you get a lower phase, consisting of glycerol and methanol, and a superior one, containing the fatty acid methyl esters (FAME).
So taken was 1 µ L of the upper phase for gas chromatographic analysis.

3.15.1 Equipment
The determination of FAME was carried out with an Agilent Technologies 6850 Series II chromatograph equipped with capillary column of 100m, 0,25 mm ID, 0,20 µm film thickness and with a stationary phase 50% Cyanopropyl Methyl Silicone (Supelco Bellofonte, USA), a flame ionization detector, and PTV, programmed temperature vaporizer.

3.15.2 Operating conditions
PTV:
40°C for 0.10 min, rate of 500°C/min until to 270 for 5 min
Oven:
- Initial temperature 120°C for 5 min, rate of 5°C /min until to 165°C for 5 min; rate of 5 °C/min until to 240°C for 30 min.
- Split ratio: 1/60
- Gas carrier: He
- FID: mix H_2/air 1/10; 260°C

3.15.3 Identification and quantification
The peaks identification was made by external standard (SupelcoTM 37 component FAME MIX). The samples concentration was calculated by comparison with retention time of pure standard and by response factors (Rf), to convert peak areas into weight percentages.

3.15.4 Statistical analysis
All determinations and experiments were performed in triplicate, and the results presented are the average values of three determinations. The coefficient of determination (R^2) of linearity for the data was statistically analyzed using the Microsoft Excel 2000 program (Microsoft Corporation, Redmond, WA). An analysis of variance (ANOVA) was conducted using the software XLSTAT 2006, version 2006.6 (Addinsoft, Paris, France) to compare the data obtained for different frying times. Differences were considered significant at $P \leq 0.05$.

3.16 Results FA composition

In **Tabb. 3.5, 3.6 and 3.7**, the FA composition of the thermo-oxidized oil, frying oil and fat extracted from French fries after different treatment times are reported for palm superolein.
In **Tabb. 3.8, 3.9 and 3.10**, for olive oil, for sunflower oil in **Tabb. 3.11, 3.12 and 3.13**, for lard in **Tabb. 3.14, 3.15 and 3.16** and for mix oil in **Tabb.3.17, 3.18 and 3.19**.
The composition of the major fatty acids present in bi-fractionated palm oil in its fresh state was as follows: palmitic acid (C16:0), 36.13 g/100 g; oleic acid (C18:1), 45.20 g/100 g; stearic acid (C18:0), 3.40 g/100 g, linoleic acid (C18:2), 12.50 g/100 g; and linolenic acid (C18:3), 0.19 g/100 g. The UFA/SFA ratio is 1.41.

The composition of the major fatty acids present in olive oil in its fresh state was as follows: palmitic acid (C16:0), 11.36 g/100 g; oleic acid (C18:1), 71.09 g/100 g; stearic acid (C18:0), 2.62 g/100 g, linoleic acid (C18:2): 12.00 g/100 g; and linolenic acid (C18:3), 0.60 g/100 g. It is characterized by an UFA/SFA ratio of 6.05.
The sunflower oil, in its fresh state, contain: palmitic acid (C16:0), 5.53%; stearic acid (C18:0) 3.10%, oleic acid (C18:1) 31.62% and linoleic acid (C18:2) 58.49%. It is characterized by an UFA/SFA ratio of 10.32.
The lard, in its fresh state, has the following acidic composition: palmitic acid (C16:0), 21.46%; stearic acid (C18:0) 14.73%, oleic acid (C18:1) 44.77% and linoleic acid (C18:2) 12.95%. It is characterized by an UFA/SFA ratio of 1.52.
The mix oil, in its fresh state, contains 4.99% of palmitic acid, 2.42% of stearic acid, 59.92% of oleic acid, 25.70% of linoleic acid and 4.43% of linolenic acid. It is characterized by an UFA/SFA ratio of 10.77.
It is particularly interesting, in the evaluation of the effects of heat prolonged and intermittent treatment exercise on oils used, follow the trend of the fatty acid composition, in particular the evolution of the fatty acids and of ratios most significant.
The short chain fatty acid C8:0 is a secondary oxidation product that originates from the homolytic β-scission of hydroperoxides (Frankel, 2005). During the frying process, high temperatures determine the cleavage on the carbonyl side of oleate, linoleate and linolenate hydroperoxides, with consequent formation of short chain fatty acid (C7:0 or C8:0) bonded to the tracylglycerol structure and of unsaturated aldehydes (Màrquez Ruiz & Dobarganes, 1996), some of which are responsible for the "rancid " or the "fried food" smell. The saturated short-chain FAME can be proposed as a good indication of the total alteration level in frying oils because they accumulate in oil due to their high stability (Dobarganes et al., 1986).
Table 3.20 shows the methyl octanoate trend in bi-fractionated palm oil samples, during heat treatment. The C8:0 showed an increased trend, in thermo-oxidized oils and in fats extracted from French fries. About frying oil samples the C8:0 reaches a maximum at 32nd hour and then it experiences a moderate decrease. The fresh oil contains a small amount of C8:0, equal to 0.02%. In thermo-oxidized samples it reached a concentration of 0.20% at 48 h of treatment.
About olive oil, **Tab. 3.21** shows the C8:0 trend. It was not present in fresh oil, however, appeared as early as the 8th hour of heat treatment in all three samples sets, where showed a different trend with increasing time. In thermo-oxidized olive oil, methyl octanoate had a growing trend until it reached a concentration of 0.43% at the end of treatment. About frying oils and fats extracted from potatoes, there was a down trend which may be due to the interaction oil-food: the evolution of C8:0 between the two samples sets is inversely proportional. In particular, methyl octanoate was not detected at 24th, 40th and 48th frying time in the oil extracted from potatoes, while, at these hours, it present in rather high concentrations in the frying oils. **Table 3.22** shows the C8:0 trend of sunflower oil. It was absent in thermo-oxidized samples, showed a rising trend in the frying sunflower oil samples and it had a growing trend until the 32nd hour, and then decreased in samples extracted from potatoes. **Table 3.23** shows the C8:0 trend in lard. Both in the thermo-oxidized samples and in fats extracted from potatoes C8:0 appeared only at 24 hours, increased at the 32nd hour and remained constant until the end of heat treatment. In frying oil samples it appeared at 8th hour and remained constant during all the frying process. **Table 3.24** shows the C8:0 performance in the mix oil. In all three series of samples, it appeared at 8th hour and had a growing trend.
In order to assess whether the C8:0 is actually a good indicator of the frying oil oxidation, it is important to see how this molecule is related to the TPC, up to now only indicator required by current legislation. These two parameters are well correlated in samples of thermo-oxidized bi-fractionated palm oil (R^2 = 0.9134), frying (R^2 = 0.893) and extracted from potatoes (R^2 = 0.9405) (**Figg. 3.2, 3.3 and 3.4**).
In olive oil unfortunately C8:0 and TPC did not well correlate, with the exception of thermo-oxidized olive oil which had a discreet relationship with an R^2 = 0.897 (**Fig. 3.5**) compared to an index of 0.6989 for the frying olive oil (**Fig. 3.6**). This result is essentially due to the trend of C8:0, which did not grow continuously during frying.
In sunflower oil the C8:0 had a good correlation (R^2 = 0.8629) only in frying samples (**Fig. 3.9**). In lard, C8:0 had a constant trend, and it had no correlation with TPC.
Finally in mix oil the C8:0 discreetly correlated with TPC in both thermo-oxidized samples (R^2 = 0885) (**Fig. 3.13**), in frying samples (R^2 = 0.9542) (**Fig. 3.14**) and in those extracted from potatoes (R^2 = 0.9209) (**Fig. 3.15**)
Linoleic acid (C18:2 n6cis) is frequently used as an indicator of the degree of oil degradation, since the polyunsaturated linoleyl chain is highly susceptible to oxidation (Frankel, 2005).
Tabb. 3.20-3.24 show the progress of linoleic acid in the progress of the heat treatment, for the five oils used. The evolution of this fatty acid appeared to be quite similar in all the oils; in the thermo-oxidized oils its concentration decreased with increasing time of heat treatment, while for the frying oils and for fats extracted from fried potatoes, the results indicated that an exchange of lipids between fried food and fatty matrix occurred. In fact, more than 90% of the fried food lipids came from the frying oil while more than 85% of the pre fried food lipids were released into the frying oil (Dobarganes et al., 2000).

The oil extracted from frozen pre-fried potatoes, at time zero, contain 37.90% of C18: 2 n6cis, an amount far greater than that one possessed by the bi-fractionated palm oil (12.50%), olive oil (12%), lard (12.95%) and by the mix oil (25.70%), second only to the percentage present in sunflower oil (58.49%). This content sharply decreased at the 8th hour of frying already it assumes a value equal to 14.73% for potatoes fried in palm oil, to 13.86% for those fried in olive oil, 14.58% for those fried in lard and 27.41% for those fried in oil mix. The linoleic acid concentration, in the frying oil, slightly increases (olive oil) or remains the almost unchanged (bi-fractionated palm oil, lard and mix oil) because of lipid exchange between bath oil and fat content of frozen pre-fried potatoes. In sunflower oil, the situation is exactly the opposite. The sunflower oil, at time 0, has a greater C18:2 n6cis concentration than that one in the fat extracted from the pre-fried potatoes, it follows that, for frying oil samples, during the heat treatment a decrease of this fatty acid, and an increase for the fat extracted from French fries occurred.
In fact in fats extracted from French fries the C18: 2n6cis increased from 37.90, at time 0, to 55.40, at 8 hours, then this fatty acid undergoes a reduction during the following hours reaching a value of 51.10% at 48 hours.
About correlations between TPC and C18:2 n6cis, do not always get good results but more often acceptable. In the bi-fractionated palm oil the correlation indexes between TPC and C18: 2 n6cis were stood at 0.9593 for the thermo-oxidized samples (**Fig. 3.2**), 0.8233 for frying samples (**Fig. 3.3**) and 0.7124 for samples extracted from French fries (**Fig. 3.4**).
In the olive oil C18:2 n6cis had a R^2 of 0.9487 for thermo-oxidized samples (**Fig. 3.5**), 0.6889 for frying samples (**Fig. 3.6**) and 0.8297 for samples extracted from potatoes (**Fig. 3.7**).
In sunflower oil C18:2 n6cis had the following correlation indices with TPC: 0.9302 in thermo-oxidized samples (**Fig. 3.8**), 0.7776 in frying samples (**Fig. 3.9**) and 0.9287 in samples extracted from potatoes (**Fig. 3.10**).
In lard, C18:2 n6cis had a R^2 of 0.9428 in thermo-oxidized samples (**Fig. 3.11**) and 0.7782 in samples extracted from potatoes (**Fig. 3.12**).
Finally in mix oil correlation between C18:2 n6cis with TPC had an R^2 of 0.8797 in thermo-oxidized samples (**Fig. 3.13**), and 0.8885 in frying samples (**Fig. 3.14**).
The linoleic/palmitic acid ratio (C18:2 n6cis/C16:0) can be used to evaluate the extent of oil oxidative degradation during the frying process (Bansal et al., 2010). In all five oils used, the linoleic acid is the major polyunsaturated fatty acid and the palmitic acid is the major saturated fatty acid.
The ratio between these two fatty acids appeared to be decreased during heat treatment in bi-fractionated palm oil, olive oil, sunflower oil and mix oil both thermo-oxidized and frying. This reduction appears more evident in thermo-oxidized samples than in frying ones (**Tabb. 3.20-3.24**).
Both the thermo-oxidized and frying lard samples showed a moderate increase in C18:2 n6cis/C16:0 ratio during the experimentation time. Both the super palm olein and olive oil extracted from French fries showed a decrease, the same goes for sunflower oil and mix oil if the value of this index at time 0 was excluded.
The C18:2 n6cis/C16:0 had a particular trend for lard extracted from French fries, it decreased at 8th hour, then increased until 16 hours, decreased at 24th hour, increased at 32nd hour and decreased at 40th hour maintaining a constant value until 48 hours.
About correlations between this ratio and TPC in super palmolein, the R^2 index was 0.9715 (**Fig. 3.2**) for thermo-oxidized samples, 0.678 for frying samples (**Fig. 3.3**) and 0.6988 for fats extracted from French fries (**Fig. 3.4**).
In olive oil samples the C18:2 n6cis/C16:0 ratio well correlated with TPC (R^2 0.9461) (**Fig. 3.5**) for thermo-oxidized samples, a little less well in frying samples (R^2 0.7176) (**Fig. 3.6**) and (R^2 0.8297) in fats extracted from potatoes (**Fig. 3.7**).
In sunflower oils the correlations between this ratio and TPC were discreet in thermo-oxidized samples (R^2 0.8388) (**Fig. 3.8**), good in frying samples (R^2 0.9885) (**Fig. 3.9**) and in fats extracted from French fries (R^2 0.9155) (**Fig. 3.10**).
In lard, only samples extracted from French fries showed a correlation with TPC but not very good (R^2 0.7446) (**Fig. 3.12**).
Trans fatty acids are present in the human diet as a consequence of heat treatment of fat and oil. However, there is non consensus about if frying can be considered or not an important source of trans fatty acids. In most unprocessed foods, the proportion of *trans* fatty acids is very low to non-existent but during partial hydrogenation of oil to make margarines, shortenings, and frying oils, some of the *cis* fatty acids are converted to *trans* isomers.
Some authors have referred to as the frying process is responsible to increase the intake of trans fatty acids in the diet, by checking the existence of a link between oxidative and thermal alteration of unsaturated oils and the accumulation of trans fatty acids in these oils during heating or frying (Romero et al., 2000). According to the SINU (Italian Society of Human Nutrition) trans fatty acids in the diet should not exceed 5g/die. The intake of trans fatty acids in the Italian has averaged only 1.3 g/day, compared to 5-10 g found in countries with high consumption of hydrogenated fats (USA, Canada, Germany, Sweden and UK) (Pizzoferrato & Nicoli, 1994).

Trans fatty acids identified and quantified, in oils used, are two: the C18: 1 n9 trans, C18: 2 n6 trans-9, trans-12. The sum of these trans fatty acids is always maintained at concentrations well below 1%. They are therefore very low values that do not allow defining the frying process with unsaturated and non-hydrogenated oils, as a major source of trans fatty acids, according with other authors (Romero et al., 2000, Tsuzuki et al., 2010).
In bi-fractionated palm oil, this sum appeared to be increased with increasing time of heat treatment, reaching a maximum of 0.57%, 0.43% and 0.40% in the thermo-oxidized oils, frying oils and in fat extracted from French fries respectively (**Tab. 3.20**).
Trans fatty acids were not detected in the fresh olive oil, and in the oil extracted from potatoes at time 0, while the bi-fractionated, at time 0, showed them at a very small percentage (0.06%) (**Tab. 3.21**).
In olive oil the total content of trans fatty acids remained almost unchanged during the heat treatment, which amounted to around 0.11% both in the frying oil and in fats extracted from potatoes, while in the thermo-oxidized samples it reached a value of 0.15% at 8th treatment hour.
In sunflower oil, in all three samples sets, the Σtrans had ups and downs but overall increased in thermo-oxidized samples and in fats extracted from potatoes and decreased in frying ones (**Tab. 3.22**).
In lard, trans fatty acids were present at time 0 but did not appear in the subsequent hours of heat treatment in thermo-oxidized samples, but increased in the frying samples. In samples extracted from potatoes, although they were absent at time 0, they appeared at 8th hour and increased reaching the 0.68% at 48 hours (**Tab. 3.23**).
In mix oil the Σtrans increased from 0.02%, at time 0, to 0.61% at 48 hours, in thermo-oxidized samples, to 0.20% in frying samples and to 0.36% in those extracted from potatoes (**Tab. 3.24**).
In particular, good correlations were observed between the TPC and Σtrans in bi-fractionated palm oil samples (**Figg. 3.2, 3.3 and 3.4**), with R^2 values of 0.9420 in thermo-oxidized samples, 0.9523 in frying samples and 0.9363 in those extracted from potatoes.
In all other samples of oil were not found good correlations.
Another good marker of the heat treatment undergone by the oil in a frying is the ratio UFA/SFA. This ratio decreased in bi-fractionated palm oil samples, in thermo-oxidized and in frying olive oil samples, in sunflower oil samples (both thermo-oxidized and frying), in lard (both frying and extracted from potatoes samples) and in mix oil samples.
The correlation degree of this ratio with TPC showed good results in the thermo-oxidized bi-fractionated palm oil (R^2 0.9213) (**Fig. 3.2**), thermo-oxidized olive oil (R^2 0.9045) (**Fig. 3.5**) and frying olive oil (R^2 0.9264) (**Fig. 3.6**), in thermo-oxidized sunflower oil samples (R^2 0.8476) (**Fig. 3.8**), in frying ones (R^2 0.9392) (**Fig. 3.9**) and in sunflower oils extracted from potatoes (R^2 0.8201) (**Fig. 3.10**), in thermo-oxidized lard samples (R^2 0.9349) (**Fig. 3.11**) and in lard extracted from French fries (R^2 0.8137) (**Fig. 3.12**), and in the mix oil samples (thermo-oxidized (R^2 0.8284) (**Fig. 3.13**), frying (R^2 0.9932) (**Fig. 3.14**) and extracted from potatoes (R^2 0.8888)) (**Fig. 3.15**).

3.17 Conclusion FA composition

About fatty acid modification during discontinuous thermal treatment, the methyl octanoate was detected. This compound is a characteristic product of hydroperoxides decomposition. Good correlations were obtained between C8:0 and TPC in thermo-oxidized bi-fractionated palm oil and olive oil (R^2 0.9134 e 0.897 respectively), in frying mix oil (R^2 0.9542) and in bi-fractionated and mix oils extracted from French fries (R^2 0.9405 e 0.9209). This suggests that C8:0 could be used as a possible marker of thermal treatment correlated with TPC.
About the unsaturated fatty acids content of fried potatoes, the oil-food interactions have been clearly shown: the fat content of potatoes takes, over time, the same composition of frying bath. The French fries prepared in olive oil, sunflower oil and in lard had an increased content of unsaturated fatty acids, while the French fries cooked in bi-fractionated palm oil and in mix oil showed a decrease: the choice between these oils, with respect to this index can be based on nutritional assessments.
The ratio UFA/SFA showed good correlation in the bi-fractionated palm oil, olive oil and in lard thermo-oxidized and in olive oil, sunflower oil and mix oil of frying bath.
The trans fatty acids concentration showed an upward trend in all oils, while in olive oil, there was no evidence of a net variation of trans fatty acids, which amounted to around 0.11%. These values are very low and do not worry about in terms of food. The values of trans fatty acids in bi-fractionated palm oil samples showed good correlations with TPC (R^2 0.942 for the thermo-oxidized samples, R^2 0.9523 and 0.9363 for frying samples and

for samples extracted from potatoes respectively). Another good correlation was found between the TPC and Σtrans in lard extracted from potatoes (R^2 0.9531).
Evaluating correlation indices between fatty acids and TPC, in all samples series, it can be said that possible indicators of thermal degradation of an oil are:

- For palm superolein C8:0 eΣ trans
- For olive oil UFA/SFA
- For sunflower oil C18:2 n6cis, C18:2 n6cis /C16:0 e UFA/SFA
- For lard UFA/SFA
- For mix oil the C8:0

Because there are many variables that affect oil degradation, a specific marker may be ideal for one oil but completely useless in another.
For example, Berger (2005) reported that the TPC test was associated with problems in interpreting the quality of oils with high DG content, such as palm oil and palm olein. Typically, 6-8% DG are found in palm oil and palm olein, whereas other oils contain only 2-3% or less. As DG are measured as a fraction of TPC, it may be misleading to use TPC in judging oil quality.

3.18 VOCs determination

Lipids are the main contributors to desirable and undesirable flavors in fried foods. A variety of compounds consisting in series of aldehydes, ketones, hydrocarbons, and alcohols arise through decomposition of hydroperoxides at high temperatures. In addition to the frying oil, other important sources of volatiles include oxidative and thermal decomposition of food lipids; break down products of other main constituents of the food, and compounds produced by interaction of food components and/or interaction between food and frying oil (Maillard reaction). Such complicated mixtures of reactive components at frying temperatures give very complex flavor profiles and, hence, identification of volatiles formed by interaction of frying oils and food constituents is still a difficult task (Dobarganes et al., 2000).
The main systems to collected volatile compounds are

- Static head space (SHS)
- Dynamic head space (DHS)
- Solid phase micro-extraction (SPME)

In this study a dynamic head space analysis, purge and trap system, was used.

3.18.1 Method principle

The dynamic head space analysis, also known as “purge and trap”, is more sensitive than the static headspace method. It includes four steps: i) purging or sweeping a liquid sample with nitrogen or helium in a heated tube or vessel; ii) trapping the vaporized volatiles into a short column containing a porous polymer (Tenax, Chromosorbs or Porapaq) or charcoal with or without cooling; iii) desorbing the volatiles from the trap at elevated temperatures and transferring, by blackflushing with carrier gas, into the capillary inlet of the gas-chromatograph; and iv) separating the volatile compounds by GC. Quantification of the volatile compounds is based on the recovery of a suitable internal standard subjected to the same conditions as the sample.
In GC compounds are separated according to their characteristics of volatility. Each compound provides a signal (peak) allowing the identification of the compound on the basis of time spent to reach the detector. In the case of very complex mixtures is used gas chromatography / mass spectrometry: the molecules are affected by a high-energy electron beam that causes the dissociation into fragments characteristic of weight. Each molecule is characterized by a particular profile that can be identified.
The advantages of this method reside in the high sensitivity because the analyte is concentrated and the detection limit of molecules is of the order of ppb. It is also not necessary to wait for the establishment of equilibrium between the headspace and the sample, as in SHS, since there is continuous extraction of volatile compounds from the carrier gas.
The disadvantages of the technique are mainly related to the instrument cumbersome and difficult to use. In fact there are many parameters need to be optimized such as: the flow of carrier gas, the temperature of the sample pre-heating and heating of the trap, the time required for the process of "purification" and desorption, etc.. In addition, there are many opportunities for failure due to damage caused by the high temperatures reached, the contamination or accumulation of water in the trap hydrophobic. The system is difficult to clean, which can lead to overestimates, is important to avoid contact with oxygen to protect against oxidation and volatile compounds in the sorbent cartridge.

3.18.2 Equipment

The samples were analyzed by the Dynamic Headspace System using a "Purge & Trap" (Tekmar Instruments, Manchester, UK) (**Fig. 3.1**). This tool has three main processes:

• The Purge: allows removing the volatile substances from the sample. The "purge gas" passes through the bottom of the vessel, and the dispersion of the gas in the fine particles occurs allowing them to get in touch with a wider sample surface. This process allows the flow of inert gas stripping the analytes from the sample and concentrating them on an absorbent trap.

• The Desorb which occurs during the heating of the trap that is crossed by the gas desorption, which transfers and releases the analytes of interest to the gas chromatograph (GC). Between the trap and the GC is placed a humidity control system needed to remove water from the stream of desorbed compounds. This is important because the detectors are sensitive to water.

• The Bake: it is necessary to clean the trap before the next injection. In this process the six-port valve is closed and the flow of purge gas throughs the cartridge.

The instrument used for testing has a Tenax ® trap called poly-2,6-diphenyl *para*-phenylene oxide. The Tenax ® is one of the most widely used because it is capable of absorbing several classes of molecules, especially aromatic ones, and also can be heated even at high temperatures (250°C).

3.18.3 Operating conditions

The volatile organic compounds were isolated from frying oil using the purge and trap concentrator DHS, a model from Teledyne Tekmar Instruments (Manchester, UK) equipped with a Tenax trap. The sample (2 mL) was added with 100 μL of deodorized oil solution containing 10 ppb of undecane as an internal standard (I.S.). A purge vessel containing the sample was connected to the purge and trap unit and was subjected to a specific program (**Tab. 3.1**).

VOC analysis was performed using the Agilent 6890N gas-chromatograph equipped with an Agilent 5973 N mass spectrometer and a capillary column with 5%-phenyl-methylpolysiloxane (30 m x 0.25 mm id x 0.25 μm) HP-5 MS (Agilent J&W, Santa Clara, CA, USA). Helium was used as the carrier gas at a flow rate of 1,2 mL/min. The oven temperature program was as follows: 45°C for 3 min, 10°C/min ramp to 240°C for 1 min; and 15°C/min ramp to 270°C for 1 min. The mass spectra were generated at 70 eV in the range of 35-400 UMA. The VOC identification was achieved by comparing the mass spectra and GC retention times with those of the pure standard compounds that are available and the data system library of the GC-MS equipment (NIST 02 and WILEY 275).

3.18.4 Samples preparation

In the purge vessel the sample (2 mL) was added with 100 μL of deodorized oil solution containing undecane as an internal standard (I.S.). The internal standard respect the following criteria:

- It is not present in the mixture to be analyzed;
- It is well resolved from other components;
- Does not react with any component of the mixture.

Since the known concentration of internal standard (10 ppb) has arrived to the quantification of volatile compounds through the following relationship:

Analyte concentration (ppb) = (total area of analyte / area of absolute standard) × 10

3.18.5 Statistical analyses

All determinations and experiments were performed in triplicate, and the results presented are the average values of three determinations. The coefficient of determination (R^2) of linearity for the data was statistically analyzed using the Microsoft Excel 2000 program (Microsoft Corporation, Redmond, WA). An analysis of variance (ANOVA) was conducted using the software XLSTAT 2006, version 2006.6 (Addinsoft, Paris, France) to compare the data obtained for different frying times. Differences were considered significant at $P \leq 0.05$.

3.19 Results VOCs

Volatile organic compounds (VOCs) are a group of low molecular weight aliphatic and aromatic compounds with low boiling point. Their identification is important because they are direct responsible of fat and oil flavors.
There are three major sources of flavor in frying oils. First, naturally occurring flavor compounds in oils give distinct flavors to all oils. These distinct flavors are most noticeable after the oil is extracted or expelled from the oilseed. Processing of oil can also affect frying oil flavor. For example, when oil is hydrogenated, it develops a specific flavor that is often described as fruity, flowery, and/or milky. The greater the degree of hydrogenation, the more distinct this flavor becomes. Finally, the primary source of flavor in frying oils comes from the decomposition of the major fatty acids, oleic, linoleic, and linolenic at temperatures of approximately 180°C. Volatile compounds produced by thermal oxidation include aldehydes, ketones, alcohols, acids, esters, hydrocarbons, lactones, substitude furans, and aromatic compounds.
During the frying of foods additional products may also be derived from interactions between lipid oxidation compounds and food components (proteins and carbohydrates) (Dobarganes et al., 2000).
Gas-chromatographic analysis of fat samples after different frying treatments represent mainly the more stable volatile compounds remaining in the fats that are not removed from the oil by steam distillation and the sweeping action of steam generated during frying.
Volatiles identified and quantified in oil samples used in experimentation are listed in **Tabb. 3.25-3.39**.
In particular, their percentage contents were reported in **Tabb. 3.40-3.54**.
The volatile compounds in the frying oil are continually changing, for this reason it was not possible to identify a general trend for these compounds. They showed a randomized pattern because of the fluctuations in formation and degradation of the compounds at frying temperature. However there were some exceptions. In **Tabb. 3.55-3-58** there are some volatile organic compounds that have a more or less linear trend during the heat treatment. In particular in bi-fractionated palm the Σalkanes (**Tab. 3.55**) showed a growing trend during heat treatment and also an acceptable correlation with TPC (R^2 0.8650) (**Fig. 3.16**).
About olive oil **Tab. 3.56** shows the performances of 2,4-E,E-nonadienal, 2,4-E,E-decadienal, 2,4-E,E-dodecadienal in thermo-oxidized samples, and the trend of Σalkadienals in the thermo-oxidized and frying samples. The correlations between these VOCs and TPC are acceptable: 0.9161 for the 2,4-E,E-nonadienal, 0.8349 for the 2,4-E,E-decadienal, 0.8123 for the 2,4-E,E-dodecadienal and 0.8822 for Σalkadienals (**Fig. 3.17**) in thermo-oxidized samples, and between Σalkadienals and TPC 0.9490 in frying samples (**Fig. 3.18**).
The **Tab. 3.57** shows the performance of octanal and butyl pyrrole in the samples of thermo-oxidized sunflower oil and **Fig 3.19** reports the correlations with TPC (R^2 0.9499 for the aldehyde and 0.9905 for the pyrrole). Finally, also mix oil had volatile organic compounds with a more or less linear trend. **Table 3.58** shows the performance of 1-octen-3-ol, of octanal, 2-E-nonenal, 2-E-decenal, 2-heptanone, 2-pentyl furan, Σalkenals and Σketones. Among these, the only ones to show the best correlations were E-2-nonenal (R^2 0.7407), 2-heptanone (R^2 0.7136) and Σketones (R^2 0.8055) (**Fig. 3.20**).
The dynamics of their training, because of the presence of the food matrix, prove to be quite complex and difficult to interpret.

3.19.1 Flavors from decomposition of fatty acids

The compounds present in greater amounts are represented by the products of hydroperoxides decomposition of oleic and linoleic acids, the major unsaturated fatty acids that characterize the oily matrices. In fact high concentrations of nonanal and octanal (n-alkanals), 2-E-decenal and 2-undecenal (2-alkenals) and octane and heptane (n-alkanes) from the decomposition of the four hydroperoxides of oleic acid were detected, as you would expect from oils rich in oleic acid. Considering that the major polyunsaturated fatty acid in all the oil is linoleic acid, the VOC analysis also revealed the presence of high amounts of hexanal, 2- heptenal and 2,4-decadienal.
The isomers of 2,4-decadienal impart a desirable fried food flavor in fried potatoes when present in small amounts, but excessive amounts of this aldehyde would be expected to cause undesirable rancid flavors (Frankel, 2005).
About frying oils in their fresh state, the main VOCs classes identified were alkanes and alkanals. In bi.-fractionated palm oil the alkanals represent about the 80% of volatiles and alkanes which constitute the remaining 20%. In olive oil instead the alkanes are the main fraction, representing about 69%, while the alkanals represent about 25%, there are also small amounts of alcohol, alkenals, ketones, acids and aromatic heterocyclic compounds.
In sunflower oil the alkanes correspond to approximately 60% (59.41%) and the alkanals to 37.86%. In lard the 80.78% of the VOC is represented by alkanes and only 13,34% by alkanals. In the mix oil then all the VOCs are essentially alkanals (as much as 99.50%) and there is a very small % (only 0.20%) of alkanes.

However, just after 8 hours of heat treatment, there is an enrichment of the pattern of volatile compounds. For frying bi-fractionated palm oil occurred the formation of alkenes, alcohols, alkenals alkadienals, ketones, acids and aromatic heterocyclic compounds, while alkanes and alkanals start to decline, with a random pattern, not correlated with the degree of heat treatment (**Tab. 3.41**). The same behaviors were found also in the thermo-oxidized super palmolein (**Tab. 3.40**). **Tab. 3.55** shows the trend of Σalkanes (ppb) during heat treatment of thermo-oxidized bi-fractionated palm oil.
This quantity increases with increasing the time, so it was evaluated the correlation with TPC (**Fig. 3.16**) which seems fairly good (R^2 0.8650). About oil extracted from potatoes, it, at time 0, already contains aromatic hydrocarbons and monoterpenes, which decreases during the heat treatment. On the other hand the acids (from 5.61% to 12.79%), the alkenals (from 10.03 to 28.43) and alkanes (from 5.9 to 7.12) increase (**Tab. 3.42**). Thermo-oxidized olive oil (**Tab. 3.43**) shows a decrease of alkanes, from 68.61 to 55.13%, an increase of alkenals (from 2.61 to 11.27) while alkanals remain almost constant (from 24.93 to 24.46%). **Table 3.56** shows the trends of the 2,4-E,E-nonadienal, 2,4-E,E-decadienal, 2.4-E,E-dodecadienal and Σalkadienals in thermo-oxidized olive oil and **Fig. 3.17** shows the respective correlations with TPC (R^2 0.9161, 0.8349, 0.8123, 0.8822). The 2,4-decadienal is formed for homolytic β-cleavage of linoleic acid 9-hydroperoxide, but it can also be formed from the oleic acid, in particular by one of its decomposition products, the 2-decenal. The 2,4 alkadienals can be formed by hydroperoxidation or hydroxylation of allylic methylenic carbon of 2-alkenals produced by decomposition of oleic acid hydroperoxide, followed by loss of water or hydrogen peroxide. (Warner et al., 2001). Of course, the amount of alkadienals formed with this mechanism is much lower than that obtained directly from the cleavage of hydroperoxides. This explains why foods fried in oils with high oleic acid content have a less intense flavor of "frying"; indeed these oils produce, as a result of thermal and oxidative degradation, large amounts of 2-nonenal and 2-decenal that give them plastic and fruit smells (Neff et al., 2000). In thermo-oxidized olive oil this alkadienal decreases, this is due to its decomposition with the progress of the frying process. The 2,4-decadienal decomposes either to the 2,3-epoxy or the 4,5-epoxy derivative which further decomposes to 2-octenal and acethaldeyde or to 2-octene and glyoxal (Andrikopoulos et al., 2003). Both octenal and octane were identified among the volatile compounds.
In frying olive oil (**Tab. 3.44**), starting from the 8th hour of treatment, there is an increase of alkenals and alkanals, while alkanes are reduced and then the formation of alkadienals, absent in the oil at time 0, occurs. At the end of 48 hours of frying, there is a net reduction of alkanes, which decreased from 68%, in fresh oil, to 28%, and simultaneously the alkanals increase from an initial amount equal to 25% of the total, up to a final 55%. Again randomized trends are observed, probably due to the many decomposition reactions that make the mechanism of volatile compounds formation by lipid oxidation, extremely fragile and dynamic (Przybylski et al., 1995).
However in frying olive oil the Σalkadienals always seems to have a decreasing trend over time (**Tab. 3.56**), in fact it well correlates with TPC (R^2 0.9490) (**Fig. 3.18**).
The olive oil extracted from potatoes shows a significant increase of alkanes (from 5.09 to 18.47) and alkanals (from 33.74 to 73.94) (**Tab. 3.45**), unlike hydrocarbons are reduced significantly up to be almost absent at 48 hours and limonene, present at time 0, does not appear in the subsequent hours of heat treatment. The VOCs trends, in this set of samples, were highly randomized and for this did not allow obtaining good correlations with the TPC.
In the thermo-oxidized sunflower oil (**Tab. 3.46**) there is a reduction of alkanes (from 59.41 to 22.97) and an increase of alkanals (from 24.03 to 37.86). Among the alkanals the octanal shows an increasing trend (**Tab. 3.57**), and it well correlates with TPC (R^2 0.9499) (Fig. 3.19). A good correlation was also found for the butyl pyrrole (R^2 0.9905) (**Fig. 3.19**) whose increasingly trend is reported in **Tab. 3.57**.
In frying sunflower oil (**Tab. 3.47**) alkanes increase (from 59.41 to 70.27), the alkanals decrease (from 24.03 to 18.68), the alkenals and alkadienals increase from 4.47 to 5.16 (alkenals) and from 0.26 to 2.16 the alkadienals, and even ketones considerably reduce (from 8.81 to 0.46).
In sunflower oil extracted from potatoes (**Tab. 3.48**) alkanes (from 5.09 to 12.92), alkenals (from 10.03 to 23.35), alkadienals (from 7.30 to 17.20) and heterocyclic aromatic hydrocarbons (from 2.98 to 10.43) increase. On contrary alkanals (from 33.74 to 21), aromatic hydrocarbons (from 17.23 to 1.31) and limonene (18 to 10.76) decrease.
In thermo-oxidized lard (**Tab. 3.49**) alkanes reduce from 80.78 to 67.03, alkanals and alkenals increase (from 27.89 to 13.34 the alkanals and 2.44 to 3.42 the alkenals). Frying lard (**Tab. 3.50**) shows the same pattern observed for the thermo-oxidized samples but with more marked changes.
In lard extracted from potatoes (**Tab. 3.51**) alkanes, alkenals and alkadienals increase and alkanals, aromatic hydrocarbons decrease. At 8 hour, sulfur compounds appear. Because of too random trend of VOCs detected in lard samples volatile compounds do not showed good correlations with TPC.
In the thermo-oxidized mix oil (**Tab. 3.52**) alkanes and alkenals undergo a sharp increase from 0.20 to 51.82 (alkanes) and from 0.30 to 14.82 (alkenals). As consequence the alkanals, which, at time 0, accounted for 99.50% of the VOCs are reduced by switching to 14.11% at 48 hours. So alkenes, alcohols, alkadienals, heterocyclic aromatic hydrocarbons and ketones appear. Among all VOCs detected and quantified in **Tab. 3.58**

there are some which have reported a more or less linear trend. These VOCs include the E-2-nonenal, 2-heptanone and Σketones that showed acceptable correlations with TPC (R^2 0.7273, 0.7136 and 0.8055, respectively) (**Fig. 3.20**). In frying mix oil (**Tab. 3.53**) the alkanes (from 0.20 to 17.83) and alkenals (from 0.30 to 11.18) increase and alkanals (from 99.50 to 59.53) reduce. In mix oil extracted from French fries (**Tab. 3.54**) alkanes, alkenals and aromatic hydrocarbons increase (from 9.05 to 40.77 alkanes, from 10.03 to 14.89 alkenals and from 17.23 to 23.88 hydrocarbons) and on the other hand alkanals decrease (from 33.74 to 7.05).

3.19.2 VOCs from food-oil interaction

The α-dicarbonyl compounds formed during frying can react with amino-acids and proteins to form pyrazines, which give it a nutty or malt aroma of fried food (Negroni et al., 2001).

Different pyrazines are formed as powerful aroma compounds by the Maillard reaction and as secondary products of the Strecker degradation between α-dicarbonyl compounds and amino-acids, and by heating sugars with various amino-acids and other N-containing components of foods. The formation of pyrazines from amino acids such as isoleucine, leucine, phenylalanine and methionine needs the presence of carbonyl compounds. These are derived from glucose, which is in the form of starch in potatoes in large quantities, or by the decomposition of hydroperoxides (MacLeod & Seyyedain-Ardebili, 1981). In addition, Chun & Ho (1997), using model systems, showed that glutamine gave higher pyrazine yields.

Amino acids provide nitrogen for pyrazine formation. For glutamine and asparagine, nitrogen may be released as ammonia by deamination (loss of the α-amino group) or by deamidation (loss of the amide group). Deamination appears to be the more important mechanism in oil media, with more ammonia being released from glutamine than asparagine. For glutamine, deamidation can occur by intramolecular cyclization involving the amide group and either the carboxyl or α-amino group, whereas, for asparagine, intramolecular cyclization involving the amide and α-amino group does not occur due to steric hindrance. In bi-fractionated palm oil extracted from French fries the 2,5-dimethyl pyrazine was detected at 8^{th} hour of heat treatment, while in olive oil extracted from potatoes the same compounds were detected at 24^{th}, 32^{nd}, and 40^{th} hour of thermal process. In sunflower oil extracted from French fries (**Tab. 3.33**) other pyrazines were identified: the methyl pyrazine (at 8^{th} and 16^{th} hour), the 2,5-dimethyl pyrazine (from 8^{th} to 40^{th} hour with an increased trend), and the ethyl pyrazine at 8^{th} and 40^{th} hour.

The lard extracted from potatoes (**Tab. 3.36**) shows a larger number of differently methylated pyrazines: the 2,5-dimethyl pyrazine (from 8 to 40 hours, with an increased trend until 32^{nd} hour and then a decreased trend until 40^{th} hour), the ethyl pyrazine (at 8, 16 and 24 hour always increasing), the 2-ethyl, 5-methyl pyrazine (with an increased trend from 16^{th} to 32^{nd} hour) and the 3-ethyl-2,5-dimethyl pyrazine (from 8 to 40 hours). In mix oil extracted from French fries (**Tab. 3.39**) did not appear pyrazines.

The bi-fractionated palm oil extracted from potatoes showed, at 8^{th} hour, the 2-methylbutanoic acid, the corresponding acid of 2-methylbutanal resulting from the Strecker degradation. Hoffman et al. (2000) reported that these acids are formed during the Strecker degradation, but in quantities less than the respective aldehydes. The fat extracted from potatoes fried in olive oil and in lard showed a further degradation product of the Strecker aldehydes, the 1-methylethyl disulfide. In particular, from the reaction between glucose and methionine is formed methionale, a classical Strecker aldehydes, which can degrade to methanethiol which in turn produces n-alkyl sulfides. It has also been shown that oxidized lipids in the presence of methionine are easily oxidized to methionine sulfoxide, from which are formed alkyl sulfides (Yu & Ho, 1995).

3.19.3 Aromatic VOCs

Among hydrocarbons identified in vegetable oils subjected to frying process, several aromatic compounds, such as alkylbenzenes and alkylfurans, were detected.

In fat extracted from French fries the xylene (1,2-dimethylbenzene) was identified in all five oils. In bi-fractionated palm oil (**Tab. 3.27**) 2-pentyl-furan was detected. In olive oil extracted from potatoes (**Tab. 3.30**) other two benzene derivatives were detected: ethylbenzene and naphthalene (a polycyclic aromatic hydrocarbon) and 2-pentyl furan.

In sunflower oil extracted from French fries (**Tab. 3.33**) other compounds were identified and quantified: the 1,3,5 trimethyl benzene and the 1-methyl-2-(1-methylethyl)-benzene with an increased trend from 8 to 24 hours.

In lard extracted from potatoes (**Tab. 3.36**) the ethylbenzene (from 8 to 48 h), the styrene (at 0, 8, 24 and 48 h), the 2-methyl-decahydro-naphthalene and the 1,6-dimethyl decahydro naphthalene both with an increasing trend from 8 to 32h and the 2-pentyl furan.

In mix oil extracted from French fries (**Tab. 3.39**) several benzene derivatives were identified: the 2-methyl decahydro naphthalene and the 2(3H) dihydro furanone.

In bi-fractionated palm oil extracted from potatoes the styrene (vinylbenzene) was detected and quantified. Styrene is already present in the oil extracted from potatoes at time zero at a concentration of 2.45 ppb. In the bi-

fractionated palm oil, it increased until the 40th hour of frying reaching a value of 6.58ppb, and then decreased at 48 hours (**Tab. 3.27**).
The main source of public exposure to oral doses of styrene was estimated to be from its migration from polymer packaging materials (Tang et al., 2000). The amount migrated increased with the fat content of the food because of the good lipid solubility of styrene (Franz et al., 1994; Linssen & Reitsma, 1995; Tawfik & Huyghebaert, 1998). However, there is also a possible mechanism for the formation of styrene from trans, trans-2,4-decadienal. This justifies the presence of styrene in samples fried in palm olein and its absence in all other samples. In fact the 2,4-decadienal decomposed either to the 2,3-epoxy or the 4,5-epoxy derivative which further decomposed to 2-octenal and acethaldeyde or to 2-octene and glyoxal (Andrikopoulos et al., 2003). It is the methyl glyoxal that interact with L-phenylalanine and leads to the formation of styrene through the formation of two intermediate products. Two intermediates, i.e. 1-phenethylaminopropan-2-one and 2-phenylethylamine, play a role in the formation of styrene, the latter of more importance in high-moisture systems, whilst the former favours the release of styrene in low-moisture systems.
Benzene, and other derived VOCs such as alkylbenzenes, xylene and styrene, are human carcinogen and neurotoxin (Andersen et al., 2000). However, the amounts of these VOCs found in French fries are far below the amounts required to be toxic. In addition benzene toxicity is almost always associated with inhalation of vapors (Fleming-Jones & Smith, 2003).

3.20 Conclusion VOCs

Unfortunately, the VOCs determination showed a time-independent variation in the concentration of most of these compounds. The volatile compounds formation is strongly dependent on the initial composition of the fat, the greater the degree of unsaturation, the greater the number of substances that are produced. The lowest number of peaks identified in bi-fractionated palm oil, and in particular in the samples extracted from potatoes, compared to other oils, can be attributed to the higher content of saturated fatty acids that break down more difficult than unsaturated ones. This indicates a less rich sensory profile of potato fried in palm oil compared to French fries cooked in other oily matrices.
In conclusion there is no VOC that applies to all kind of oil, but for each there are one or more compounds with a good and/or good enough correlation with the TPC. In conclusion, the work wanted to show that it is not correct to use the same indicator for all lipid matrices but, on the basis of the fatty acid composition of the oil or fat used in frying, choose among those proposed, the indicator that best suits it.

3.21 References

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FIGURES AND TABLES

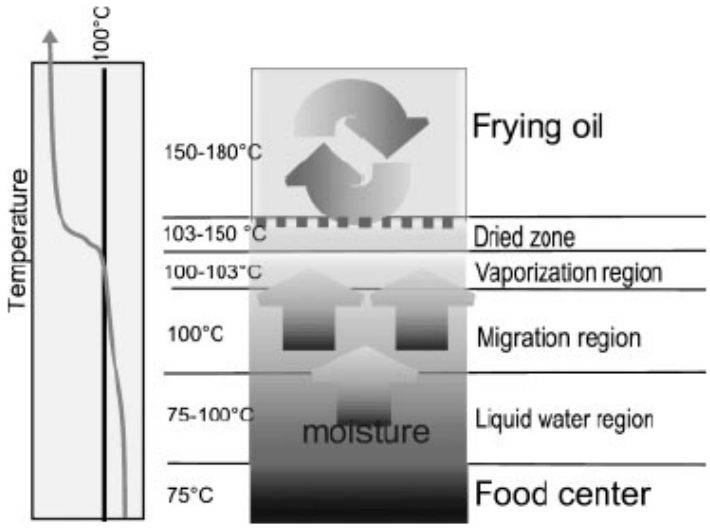

Fig. 1.1 Mass and heat transfer during frying process

Tab. 1.1- Main alterations and respective compounds produced during frying process.

Alteration	Cause	Synthetized molecules
oxidative	air	oxidized monomers oxidized dimers and polymers short-chain fatty acids volatile compounds (hydrocarbons, aldehydes, setone, alcohols, acids, etc.)
thermal	T°C	cyclic monomers dimers and polymers geometric isomers
hydrolitic	UR %	free fatty acids monoacylglycerols diacylglycerols glycerol

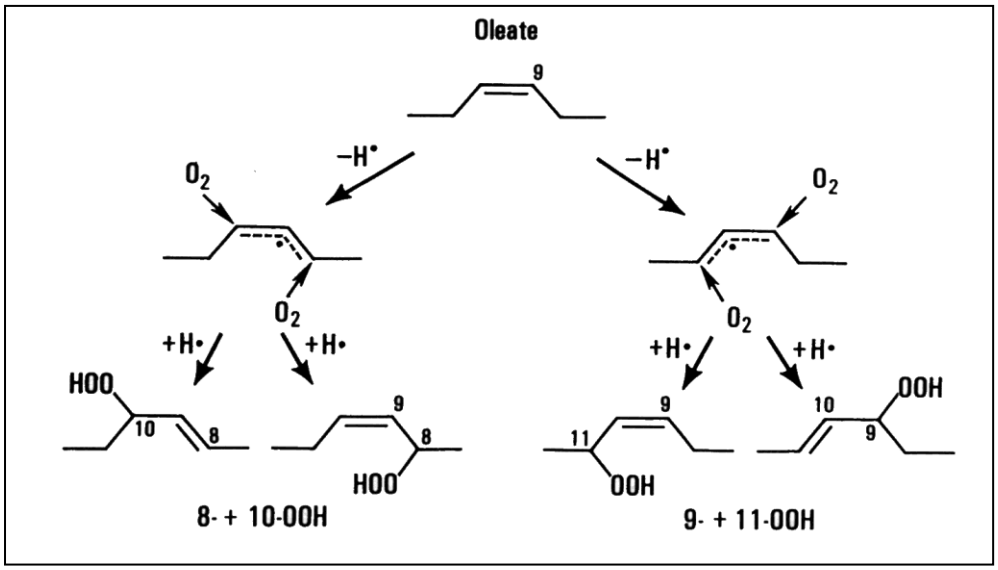

Fig. 1.2-Mechanism of oleate autoxidation

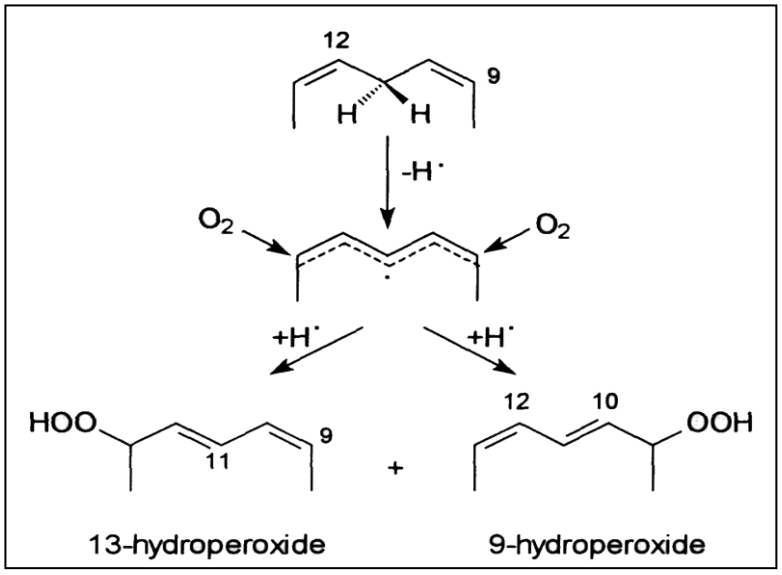

Fig. 1.3-Mechanism of linoleate autoxidation.

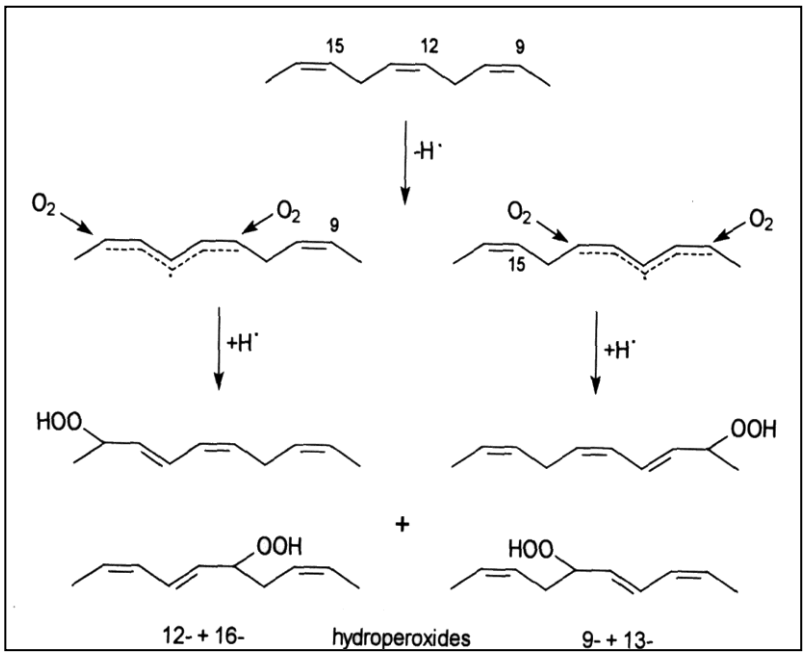

Fig. 1.4- Mechanism of linolenate autoxidation

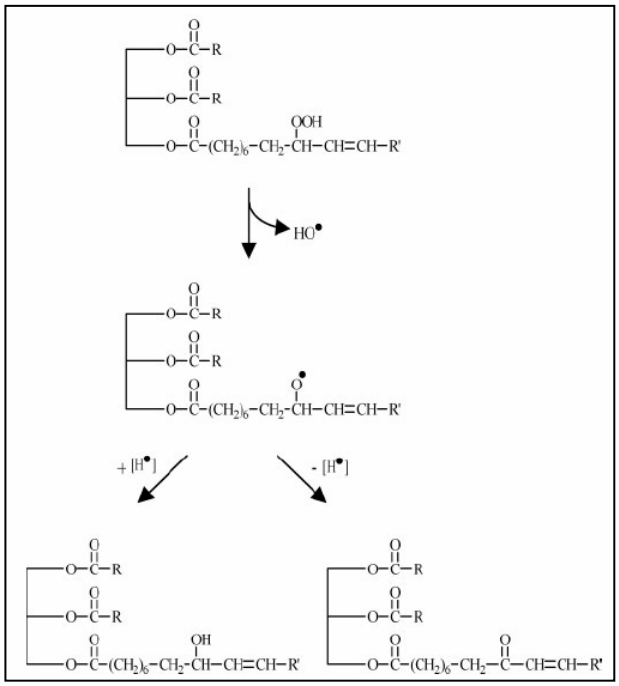

Fig. 1.5-Formation of epoxydic, hydroxylic and ketonic groups by oxidation fatty acids esterified with glycerol.

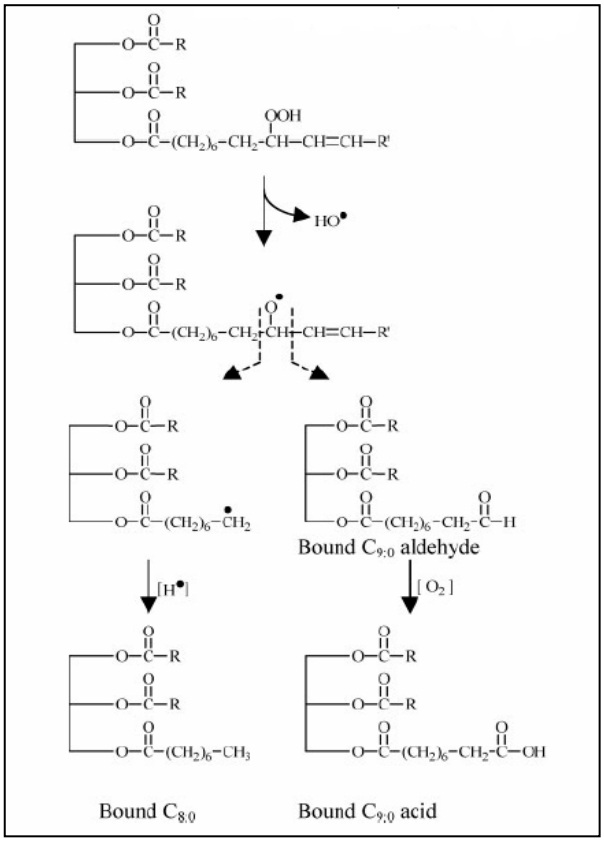

Fig. 1.6-Formation of short-chain fatty acids esterified to glycerol by decomposition of unsaturated fatty acid hydroperoxides.

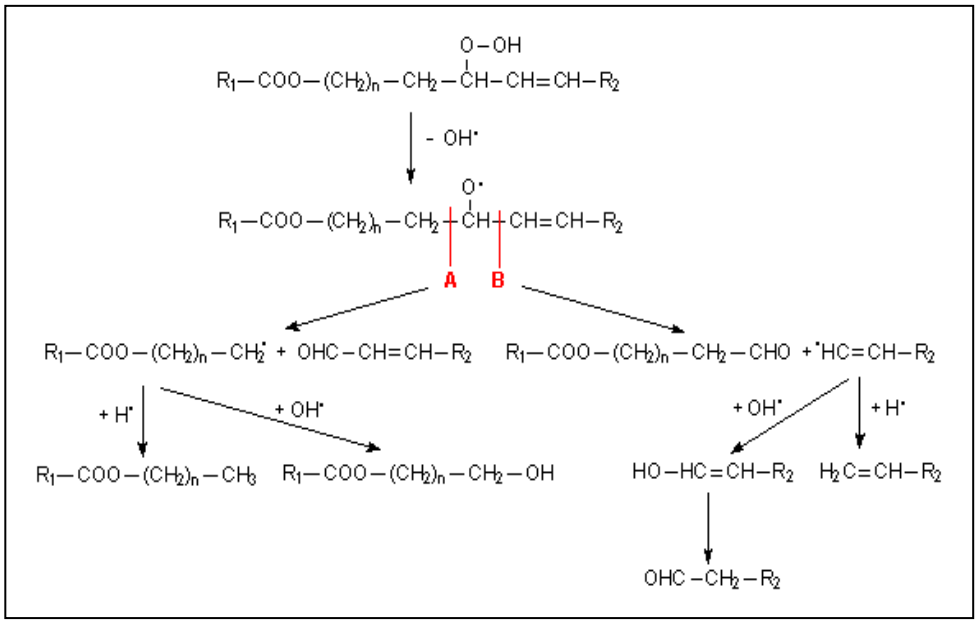

Fig. 1.7-Homolytic β-scission of fatty ester hydroperoxides.

Tab. 1.2-Volatile products formed by decomposition of hydroperoxides of oleic, linoleic and linolenic acids by a radicalic mechanism.

		Volatile compounds		
			VIA B**	
FATTY ACID	HYDROPEROXIDES	VIA*	OH·	H·
OLEIC ACID	8-OOH	2-undecenal	decanal	1-decene
	9-OOH	2-decenal	nonanal	1-nonene
	10-OOH	nonanal	octanol	octane
	11-OOH	octanal	heptanol	heptane
LINOLEIC ACID	9-OOH	2,4-decadienal	3-nonenal	1,3-nonadiene
	13-OOH	hexanal	pentanol	pentane
LINOLENIC ACID	9-OOH	2,4,7-decatrienal	3,6-nonadienal	1,3,6-nonatriene
	12-OOH	2,4-heptadienal	3-hexenal	1,3-hexadiene
	13-OOH	3-hexenal	2-pentenal	2-pentene
	16-OOH	propanal	ethanol	ethane

*Scission on bond near carboxylic function.
** Scission on bond near methylic group. Radicals produced react then with radicals OH· H· .

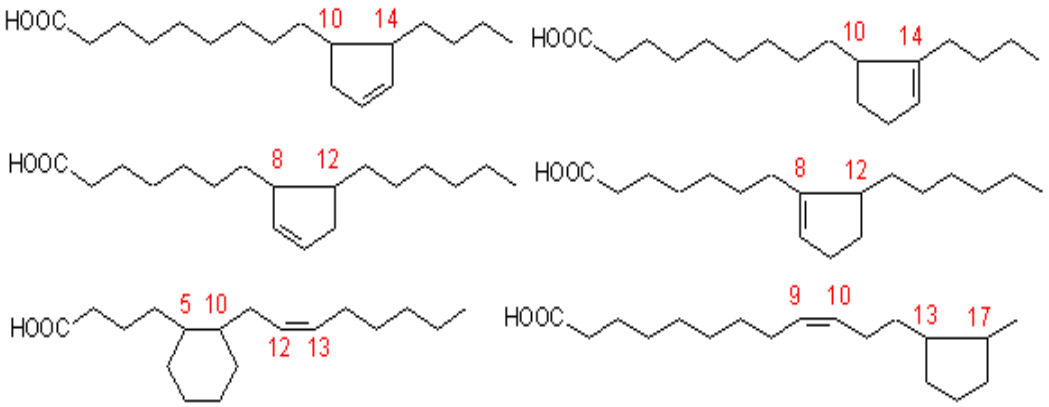

Fig. 1.8-Fatty acids produced by linoleic acid cyclization.

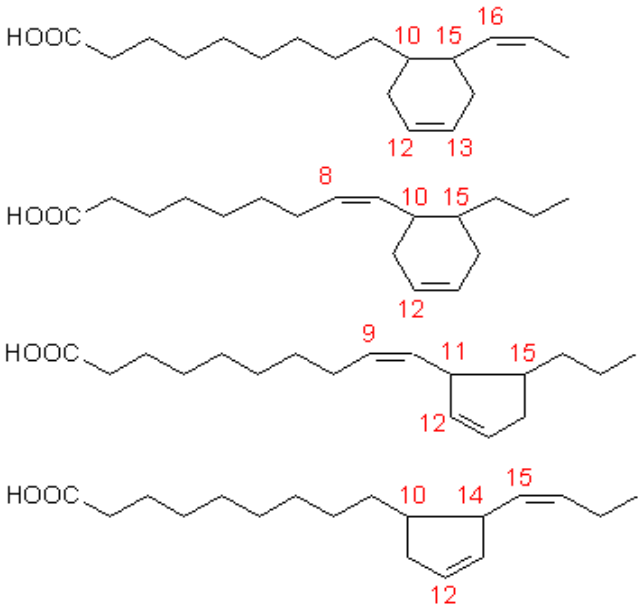

Fig. 1.9 - Fatty acids produced by linolenic acid cyclization.

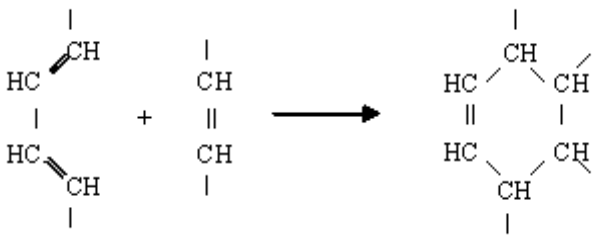

Fig. 1.10 –Non-polar dimers from Diels-Alder reaction.

Tab. 3.1-Purge and Trap conditions for volatile organic compounds determination.

"Purge"	
valve oven temp	150°C
transfer line temp	150°C
sample mount temp	90°C
purge ready temp	60°C
dry flow stanby temp	175°C
standby flow	10mL/min
pre-purge time	2 min
pre purge flow	40 mL/min
sample preheat time	3 min
preheat temp	30°C
purge time	15 min
purge temp	40°C
purge flow	40mL/min
dry purge time	2 min
dry purge temp	150°C
dry purge flow	100 mL/min
"Desorb"	
desorb preheat temp	250°C
desorb time	3 min
desorb temp	250°C
desorb flow	100mL/min
"Bake"	
bake time	10 min
bake temp	270°C
dry flow bake temp	250°C
bake flow	300 mL/min

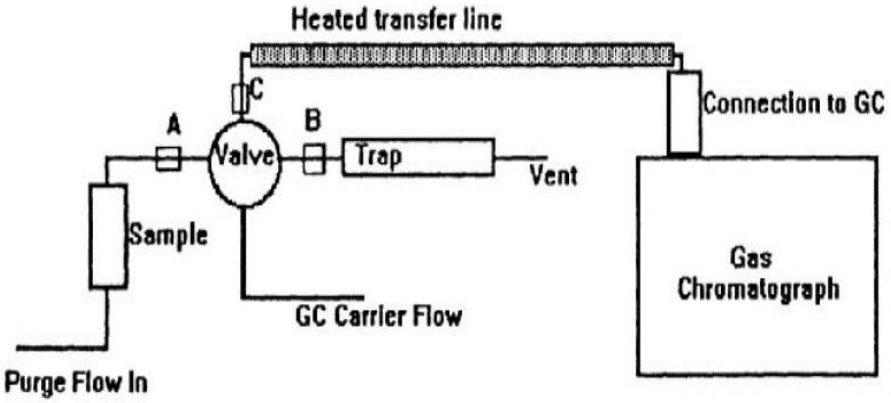

Fig. 3.1 Scheme of Purge and Trap system.

Tab. 3.2- Trend of FFA (g/100g oleic aicd) in bi-fractionated palm oil, olive oil, sunflower oil, lard and mix oil at different tratment times (thermo-oxidation, frying and extraction from French fries).

FREE FATTY ACIDS															
	Thermo-oxidation					Frying					French fries extraction				
Time (h)	palm	olive	sunflower	lard	mix	palm	olive	sunflower	lard	mix	palm	olive	sunflower	lard	mix
0	0.16±0.02	0.42±0.08	0.57±0.01	0.84±0.04	0.14±0.02	0.16±0.02	0.31±0.08	0.57±0.01	0.61±0.04	0.14±0.02	0.32±0.07	0.32±0.07	0.32±0.07	0.32±0.07	0.32±0.07
8	0.39±0.11	0.79±0.12	0.41±0.07	0.57±0.02	0.15±0.08	0.38±0.12	0.40±0.10	0.57±0.11	0.51±0.04	0.69±0.11	0.70±0.10	0.87±0.09	0.86±0.03	1.04±0.05	0.52±0.03
16	0.54±0.16	0.84±0.17	0.56±0.11	0.57±0.03	0.52±0.05	0.65±0.25	0.53±0.09	0.86±0.07	0.64±0.08	0.70±0.07	0.70±0.14	0.73±0.18	0.86±0.11	1.19±0.07	0.82±0.11
24	0.78±0.23	0.99±0.26	0.51±0.08	0.56±0.05	0.61±0.11	0.90±0.16	0.66±0.13	0.85±0.09	0.83±0.05	0.76±0.05	0.97±0.21	0.84±0.21	1.15±0.08	1.27±0.08	0.94±0.09
32	0.96±0.19	1.12±0.08	0.70±0.06	0.70±0.08	0.76±0.07	1.20±0.05	0.78±0.21	0.86±0.15	1.10±0.13	1.10±0.13	1.12±0.19	0.87±0.11	1.15±0.13	1.45±0.1	1.03±0.13
40	0.95±0.09	1.02±0.09	0.71±0.05	0.68±0.13	0.77±0.06	1.33±0.18	1.02±0.29	1.15±0.12	1.54±0.09	1.23±0.08	1.24±0.29	0.94±0.09	1.44±0.11	1.74±0.15	1.30±0.12
48	1.09±0.13	1.17±0.14	0.84±0.02	0.70±0.12	0.88±0.13	1.83±0.21	3.21±0.17	1.15±0.06	2.03±0.11	1.53±0.06	1.67±0.31	1.13±0.13	1.44±0.08	1.85±0.13	1.35±0.08

Tab. 3.3- Trend of PV (mEq O_2/Kg olio) in bi-fractionated palm oil, olive oil, sunflower oil, lard and mix oil at different tratment times (thermo-oxidation, frying and extraction from French fries).

PEROXIDE VALUE															
	Thermo-oxidation					Frying					French fries extraction				
Time (h)	palm	olive	sunflower	lard	mix	palm	olive	sunflower	lard	mix	palm	olive	sunflower	lard	mix
0	4.99±0.21	0.45±0.05	3.14±0.03	0.94±0.05	0.64±0.09	4.99±0.21	2.40±0.05	3.14±0.03	6.67±0.05	0.64±0.09	5.30±0.09	5.30±0.09	5.30±0.09	5.30±0.09	5.30±0.09
8	2.75±0.10	3.69±0.23	5.03±0.12	5.84±0.11	0.59±0.07	4.54±0.24	3.41±0.13	2.38±0.21	3.35±0.07	5.23±0.05	10.43±0.10	18.40±0.54	21.32±0.21	12.44±0.05	5.44±0.10
16	2.90±0.15	5.40±0.15	5.34±0.05	7.14±0.09	1.40±0.11	3.39±0.31	4.08±0.09	2.26±0.06	4.35±0.09	5.71±0.04	8.84±0.36	14.54±0.35	22.16±0.15	6.73±0.08	32.50±0.08
24	2.80±0.21	6.19±0.71	6.23±0.21	9.24±0.15	0.95±0.18	3.13±0.12	6.99±0.46	1.41±0.31	3.38±0.08	7.76±0.11	13.10±0.21	25.11±0.62	22.60±0.13	8.07±0.11	26.60±0.15
32	3.09±0.29	4.42±0.35	6.29±0.19	10.69±0.14	1.94±0.14	2.36±0.13	4.47±0.85	0.95±0.08	3.72±0.13	7.92±0.12	13.80±0.29	8.61±0.21	22.60±0.06	7.46±0.15	31.60±0.16
40	2.85±0.18	4.67±0.54	5.15±0.08	13.43±0.21	1.96±0.08	5.27±0.81	2.74±0.98	0.95±0.11	2.24±0.11	6.31±0.21	12.11±0.13	22.93±0.67	22.60±0.11	3.29±0.19	15.50±0.11
48	2.75±0.16	4.58±0.13	6.74±0.06	9.52±0.13	2.00±0.11	4.82±0.65	3.95±1.03	1.70±0.16	2.52±0.06	5.00±0.19	9.27±1.10	7.68±0.88	21.73±0.08	3.32±0.09	18.90±0.07

Tab. 3.4- Trend of TPC (%) in bi-fractionated palm oil, olive oil, sunflower oil, lard and mix oil at different tratment times (thermo-oxidation, frying and extraction from French fries).

TPC															
	Thermo-oxidation					Frying					French fries extraction				
Time (h)	palm	olive	sunflower	lard	mix	palm	olive	sunflower	lard	mix	palm	olive	sunflower	lard	mix
0	11.70±0.21	3.92±0.15	3.50±0.03	2.72±0.02	7.00±0.06	11.70±0.21	3.92±0.15	3.50±0.03	2.72±0.02	7.00±0.06	2.90±0.09	2.90±0.09	2.90±0.09	2.90±0.09	2.90±0.09
8	17.87±0.13	8.97±0.21	17.80±0.08	4.75±0.09	10.20±0.05	15.47±0.21	8.61±0.26	9.98±0.01	5.50±0.07	7.24±0.10	10.16±0.13	10.10±0.13	15.78±0.11	14.05±0.10	5.93±0.11
16	20.90±0.59	17.32±0.13	21.98±0.05	9.32±0.05	12.95±0.03	21.69±0.34	11.67±0.33	17.57±0.08	8.80±0.02	10.61±0.05	20.40±0.24	10.74±0.21	17.74±0.05	16.73±0.09	8.95±0.05
24	24.84±0.78	18.20±0.41	24.91±0.11	8.56±0.01	15.84±0.06	24.74±0.56	16.42±0.13	18.76±0.07	16.83±0.05	13.46±0.04	20.70±0.31	10.78±0.79	20.47±0.08	17.62±0.07	12.20±0.06
32	29.25±0.89	32.72±0.51	31.15±0.09	16.10±0.03	20.37±0.04	26.04±0.29	17.19±0.21	20.41±0.04	18.41±0.08	15.68±0.09	22.90±0.12	14.24±0.64	25.03±0.04	19.44±0.08	14.89±0.08
40	30.70±1.03	34.30±0.67	33.41±0.06	21.95±0.07	26.66±0.11	28.10±0.35	25.33±0.67	20.78±0.09	10.70±0.04	18.16±0.03	23.46±0.21	16.15±0.56	25.21±0.03	21.74±0.05	17.91±0.09
48	30.20±1.21	37.80±0.99	37.41±0.04	27.80±0.05	47.61±0.09	28.50±1.13	24.60±0.79	23.41±0.10	12.57±0.11	20.58±0.06	22.45±1.06	21.72±1.02	24.42±0.07	24.01±0.03	22.57±0.10

Tab. 3.5- Fatty acid composition (%) of thermo-oxidized bi-fractionated palm oil at different treatment times.

	THERMO-OXIDIZED BI-FRACTIONATED PALM OIL						
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	0.02^{a} ±0.00	0.04^{ab} ±0.00	0.09^{bc} ±0.00	0.12^{cd} ±0.02	0.14^{d} ±0.01	0.16^{de} ±0.02	0.20^{e} ±0.01
C10:0	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01
C12:0	0.28 ± 0.08	0.24 ± 0.00	0.25 ± 0.02	0.26 ± 0.01	0.26 ± 0.01	0.26 ± 0.01	0.26 ± 0.01
C14:0	1.15 ± 0.08	1.16 ± 0.00	1.22 ± 0.03	1.23 ± 0.02	1.22 ± 0.01	1.23 ± 0.03	1.25 ± 0.00
C15:0	0.04 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.01
C16:0	36.13^{a} ± 0.98	36.28^{ab} ± 0.13	37.59^{abc} ± 0.63	38.19^{bc} ± 0.57	38.16^{bc} ± 0.14	38.70^{c} ± 0.27	39.29^{c}± 0.14
C16:1	0.23 ± 0.01	0.21 ± 0.00	0.22 ± 0.01	0.21 ± 0.00	0.21 ± 0.00	0.21 ± 0.00	0.21 ± 0.00
C17:0	0.09 ± 0.01	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.10± 0.00
C17:1	0.03 ± 0.00	0.03 ± 0.00	0.02 ± 0.02	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00	0.03 ± 0.00
C18:0	3.40^{a} ± 0.12	3.61^{ab} ± 0.01	3.62^{ab} ± 0.07	3.67^{bc} ± 0.07	3.83^{bcd} ± 0.00	3.89 ^{cd} ± 0.05	3.94^{d} ± 0.01
C18:1n9t	0.06^{a} ± 0.00	0.16^{b} ± 0.01	0.22^{c} ± 0.02	0.29^{d} ± 0.01	0.39^{e} ± 0.01	0.47^{f} ± 0.01	0.52^{g} ± 0.01
C18:1n9c	45.20 ± 0.86	45.60 ± 0.09	45.13 ± 0.54	45.11 ± 0.40	45.49 ± 0.10	45.33 ± 0.26	45.16 ±0.06
C18:2n6t	-	0.01^{a} ± 0.00	0.01^{a} ± 0.00	0.03^{b} ± 0.01	0.03^{bc} ± 0.00	0.03^{bc} ± 0.00	0.04^{c} ± 0.00
C18:2n6c	12.50^{a} ± 0.18	11.64^{b} ± 0.01	10.63^{c} ± 0.06	9.93^{d} ± 0.06	9.25^{e} ± 0.04	8.67^{f} ± 0.01	8.09^{g} ± 0.02
C20:0	0.28^{a} ± 0.04	0.32^{ab} ± 0.01	0.32^{ab} ± 0.01	0.31^{ab} ± 0.03	0.34^{ab} ± 0.00	0.36^{b} ± 0.01	0.35^{b} ± 0.00
C18:3n6	0.05^{a} ± 0.00	0.04^{b} ± 0.00	0.04^{b} ±0.00	0.03^{c} ± 0.00	0.03^{c} ± 0.00	0.02^{d} ± 0.00	0.02^{d} ± 0.00
C20:1	0.19 ± 0.02	0.17 ± 0.00	0.16 ± 0.02	0.17 ± 0.01	0.17 ± 0.00	0.18 ± 0.01	0.17 ± 0.00
C18:3n3	0.19^{a} ± 0.00	0.14^{b} ± 0.00	0.11^{c} ± 0.00	0.10^{d} ± 0.01	0.08^{e} ± 0.00	0.07^{ef} ± 0.00	0.06^{f} ± 0.00
C22:0	0.05 ± 0.01	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.02	0.06 ± 0.00	0.07 ± 0.01	0.06 ± 0.00
C20:4n6	0.05 ± 0.02	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.01
C23:0	-	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
C24:0	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.02	0.06 ± 0.00	0.08 ± 0.00	0.08 ± 0.00
C24:1	-	0.02 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	-	-
C22:6n3	-	0.01 ± 0.00	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.00	0.03 ± 0.00	0.03 ± 0.01
SFA	41.51^{a} ±0.99	41.94^{a} ±0.11	43.39^{ab}±0.60	44.06^{bc} ±0.49	44.26^{bc} ± 0.15	44.93^{bc} ±0.26	45.63^{c} ±0.10
MUFA	45.71 ±0.83	46.19 ± 0.09	45.76 ±0.55	45.82 ±0.41	46.30 ± 0.10	46.22 ±0.27	46.10 ±0.07

PUFA	12.79^{a} ±0.16	11.87^{b} ± 0.01	10.85^{c} ± 0.04	10.13^{d} ± 0.08	9.44^{e} ±0.04	8.85^{f} ±0.01	8.26^{g} ± 0.03
UFA	58.49^{a} ±0.99	58.06^{a} ±0.11	56.61^{ab} ±0.60	55.94^{bc} ±0.49	55.74^{bc} ±0.15	55.07^{b}c±0.26	54.37^{c} ±0.10
ΣTRANS	0.06^{a} ± 0.00	0.17^{b} ± 0.01	0.23^{c} ± 0.02	0.32^{d} ± 0.01	0.42^{e} ± 0.01	0.50^{f} ± 0.01	0.57^{g} ± 0.01
C18:2 n6c/C16:0	0.35^{a} ± 0.01	0.32^{b} ± 0.00	0.28^{c} ± 0.01	0.26^{cd} ± 0.01	0.24^{de} ± 0.00	0.22^{ef} ± 0.00	0.21^{f} ± 0.00
MUFA/SFA	1.10^{a} ± 0.05	1.10^{a} ± 0.01	1.05^{ab} ± 0.03	1.04^{ab} ± 0.02	1.0^{ab} ± 0.01	1.03^{ab} ± 0.01	1.01^{b} ±0.00
PUFA/SFA	0.31^{a} ± 0.01	0.28^{b} ± 0.00	0.25^{c} ± 0.00	0.23^{d} ± 0.00	0.21^{de} ± 0.00	0.20^{ef} ± 0.00	0.18^{f} ± 0.00
UFA/SFA	1.41^{a} ± 0.06	1.38^{a} ± 0.01	1.31^{ab} ± 0.03	1.27^{bc} ± 0.03	1.26^{bc} ± 0.01	1.23^{bc} ± 0.01	1.19^{c} ± 0.00

a-g: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

Tab. 3.6- Fatty acid composition (%) of frying bi-fractionated palm oil at different treatment times.

FRYING BI-FRACTIONATED PALM OIL							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	0.02^{a} ± 0.00	0.05^{ab} ± 0.01	0.08^{bc} ± 0.01	0.12^{cd} ± 0.02	0.18^{e} ± 0.03	0.16^{de} ± 0.01	0.15^{de} ± 0.00
C10:0	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.03 ± 0.01	0.02 ± 0.00	0.02 ± 0.00
C12:0	0.28 ± 0.08	0.24 ± 0.01	0.24 ± 0.02	0.25 ± 0.00	0.30 ± 0.08	0.24 ± 0.01	0.24 ± 0.00
C14:0	1.15 ± 0.08	1.13 ± 0.02	1.15 ± 0.01	1.16 ± 0.02	1.36 ± 0.28	1.18 ±0.05	1.16 ± 0.01
C15:0	0.04 ± 0.01	0.04 ± 0.00	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.02	0.04 ± 0.00	0.04 ± 0.00
C16:0	36.13 ± 0.98	35.83 ± 0.31	36.43 ± 0.06	36.78 ± 0.41	39.99 ± 2.19	37.62 ± 1.40	37.03 ± 0.02
C16:1	0.23 ± 0.01	0.21 ± 0.00	0.21 ± 0.00	0.21 ± 0.00	0.21 ± 0.05	0.20 ± 0.02	0.20 ± 0.00
C17:0	0.09 ± 0.01	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.01	0.09 ± 0.03	0.10 ± 0.01
C17:1	0.03 ± 0.00	0.05 ± 0.02	0.03 ± 0.00	0.03 ± 0.00	0.04 ± 0.03	0.03 ± 0.01	0.02 ±0.00
C18:0	3.40^{a} ± 0.12	3.62^{ab} ± 0.02	3.69^{ab} ± 0.02	3.76^{ab} ± 0.07	3.47^{ab} ± 0.16	3.76^{ab} ± 0.24	3.90^{b} ±0.00
C18:1n9t	0.06^{a} ± 0.00	0.13^{b} ± 0.00	0.19^{c} ± 0.01	0.26^{d} ± 0.01	0.27^{e} ± 0.00	0.33^{f} ± 0.00	0.40^{g} ±0.00
C18:1n9c	45.20 ± 0.86	45.62 ± 0.12	45.32 ± 0.06	44.96 ± 0.26	42.44 ± 2.10	44.27 ± 0.83	44.43 ± 0.05
C18:2n6t	-	0.02 ± 0.01	0.02 ± 0.00	0.03 ± 0.02	0.02 ± 0.00	0.05 ± 0.04	0.03 ± 0.01
C18:2n6c	12.50^{a} ± 0.18	12.07^{ab} ± 0.02	11.60^{bc} ± 0.00	11.29^{cd} ± 0.02	10.75^{d} ± 0.38	11.17^{cd} ± 0.26	11.36^{bcd} ± 0.03
C20:0	0.28 ± 0.04	0.33 ± 0.01	0.32 ± 0.01	0.34 ± 0.02	0.30 ± 0.08	0.31 ± 0.05	0.34 ± 0.00
C18:3n6	0.05^{a} ± 0.00	0.04^{b} ± 0.00	0.03^{c} ± 0.00	0.03^{c} ± 0.00	0.03^{c} ± 0.00	0.03^{c} ± 0.00	0.03^{c} ± 0.00
C20:1	0.19 ± 0.02	0.26 ± 0.12	0.17 ± 0.00	0.33 ± 0.01	0.14 ± 0.01	0.16 ± 0.02	0.17 ± 0.00
C18:3n3	0.19^{a} ± 0.00	0.01^{b} ± 0.00	0.12^{c} ± 0.00	0.02^{b} ± 0.00	0.10^{d} ± 0.02	0.09^{d} ± 0.00	0.09^{d} ± 0.00
C22:0	0.05^{a} ± 0.01	0.07^{ab} ± 0.01	0.07^{abc} ± 0.00	0.09^{bc} ± 0.02	0.07^{abc} ± 0.01	0.09^{bc} ± 0.02	0.11^{c} ± 0.00
C20:4n6	0.05 ± 0.02	0.05 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.04 ± 0.02	0.03 ± 0.01	0.02 ± 0.00
C23:0	-	0.03 ± 0.01	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.00
C24:0	0.04 ± 0.01	0.06 ±0.00	0.06 ± 0.00	0.07 ± 0.01	0.05 ± 0.00	0.06 ± 0.02	0.08 ± 0.00
C24:1	-	0.02 ± 0.00	0.01± 0.00	0.01 ± 0.00	-	-	-
C22:6n3	-	0.01 ± 0.00	0.01 ± 0.00	0.03 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.06 ± 0.00
SFA	41.51^{a} ±0.99	41.52^{a} ± 0.28	42.25^{ab} ± 0.05	42.76^{ab} ± 0.28	45.91^{b} ± 2.37	43.61^{ab} ± 1.11	43.20^{ab} ± 0.03
MUFA	45.71 ± 0.83	46.28 ± 0.26	45.94 ± 0.06	45.80 ± 0.26	43.11 ± 2.03	44.97 ± 0.87	45.22 ± 0.05

PUFA	12.79^{a} ±0.16	12.20^{ab} ± 0.02	11.81^{bc} ± 0.00	11.4^{cd} ± 0.02	10.99^{d} ± 0.33	11.42^{cd} ± 0.24	11.58^{bcd} ± 0.02
UFA	58.49^{a}±0.99	58.48^{a} ± 0.28	57.75^{ab} ± 0.05	57.24^{ab} ± 0.28	54.09^{b} ± 2.37	56.39^{ab} ± 1.11	56.80^{ab} ± 0.03
ΣTRANS	0.06^{a} ±0.00	0.14^{b} ± 0.01	0.22^{c} ± 0.01	0.29^{d} ± 0.02	0.30^{d} ± 0.00	0.38^{e} ± 0.04	0.43^{e} ± 0.01
C18:2 n6c/C16:0	0.35^{a} ± 0.01	0.34^{a} ± 0.00	0.32^{ab} ± 0.00	0.31^{ab} ± 0.00	0.27^{b} ± 0.02	0.30^{ab} ± 0.02	0.31^{ab} ± 0.00
MUFA/SFA	1.10 ± 0.05	1.11 ± 0.01	1.09 ± 0.00	1.07 ± 0.01	0.94 ± 0.09	1.03 ± 0.05	1.05 ± 0.00
PUFA/SFA	0.31^{a} ± 0.01	0.29^{ab} ± 0.00	0.28^{ab} ± 0.00	0.27^{bc} ± 0.00	0.24^{c} ± 0.02	0.26^{bc} ± 0.01	0.27^{bc} ± 0.00
UFA/SFA	1.41^{a} ± 0.06	1.41^{a} ± 0.02	1.37^{ab} ± 0.00	1.34^{ab} ± 0.02	1.18^{b} ± 0.11	1.29^{ab} ± 0.06	1.32^{ab} ± 0.00

a-g: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.7- Fatty acid composition (%) of bi-fractionated palm oil extracted from French fries at different treatment times.

	BI-FRACTIONATED PALM OIL EXTRACTED FROM FRENCH FRIES						
	Time (h)						
Fatty Acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	$0.06^{a} \pm 0.00$	$0.10^{b} \pm 0.01$	$0.12^{c} \pm 0.00$	$0.15^{d} \pm 0.00$	$0.15^{d} \pm 0.01$	$0.16^{d} \pm 0.00$
C10:0	-	0.03 ± 0.01	0.03 ± 0.01	0.02 ± 0.00	0.02 ± 0.00	0.02 ±0.00	0.03 ± 0.01
C12:0	0.19 ± 0.06	0.24 ± 0.00	0.27 ± 0.01	0.27 ± 0.01	0.26 ± 0.01	0.27 ± 0.02	0.25 ± 0.00
C14:0	0.97 ± 0.16	1.10 ± 0.01	1.22 ± 0.00	1.22 ± 0.02	1.23 ± 0.07	1.18 ± 0.06	0.58 ± 0.78
C15:0	-	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.01	0.04 ± 0.00	0.05 ± 0.02
C16:0	19.89^{a}±0.17	35.05^{b}±0.11	36.64^{bc}±0.12	$37.20^{c} \pm 0.18$	$37.32^{c} \pm 0.87$	$36.84^{c} \pm 0.61$	$36.18^{bc} \pm 0.01$
C16:1	0.11 ± 0.19	0.23 ± 0.03	0.21 ± 0.00	0.21 ± 0.00	0.20 ± 0.02	0.21 ± 0.00	0.20 ± 0.00
C17:0	-	0.08 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.09 ± 0.01	0.10 ± 0.00	0.10 ±0.00
C17:1	-	0.03 ± 0.00	0.03 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.02 ± 0.00	0.02 ±0.01
C18:0	$3.83^{a} \pm 0.18$	$3.61^{b} \pm 0.01$	$3.56^{b} \pm 0.03$	$3.64^{bc} \pm 0.00$	$3.64^{bc} \pm 0.16$	$3.80^{abc} \pm 0.07$	$3.96^{c} \pm 0.10$
C18:1n9t	-	$0.10^{a} \pm 0.01$	$0.21^{b} \pm 0.01$	$0.24^{b} \pm 0.01$	$0.26^{bc} \pm 0.03$	$0.34^{cd} \pm 0.03$	$0.32^{d} \pm 0.01$
C18:1n9c	$36.45^{a} \pm 0.08$	$43.74^{b} \pm 0.00$	$42.83^{b} \pm 0.08$	$42.76^{b} \pm 0.16$	$42.61^{b} \pm 0.44$	$42.60^{b} \pm 0.43$	$43.29^{b} \pm 0.57$
C18:2n6t	-	0.03 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.05 ± 0.01	0.06 ± 0.05	0.05 ± 0.02
C18:2n6c	$37.90^{a} \pm 0.11$	$14.73^{b} \pm 0.13$	$13.93^{c} \pm 0.05$	$13.29^{d} \pm 0.05$	$13.30^{d} \pm 0.14$	$13.50^{d} \pm 0.08$	$13.90^{c} \pm 0.04$
C20:0	0.41 ± 0.07	0.31 ± 0.01	0.27 ± 0.01	0.29 ± 0.00	0.28 ± 0.05	0.30 ± 0.03	0.34 ± 0.03
C18:3n6	-	$0.04^{a} \pm 0.00$	$0.03^{ab} \pm 0.00$	$0.03^{ab} \pm 0.00$	$0.03^{ab} \pm 0.00$	$0.03^{ab} \pm 0.00$	$0.03^{b} \pm 0.01$
C20:1	-	0.16 ± 0.00	0.15 ± 0.00	0.15 ± 0.01	0.14 ± 0.02	0.15 ± 0.02	0.17 ± 0.01
C18:3n3	-	$0.18^{a} \pm 0.01$	$0.17^{a} \pm 0.01$	$0.13^{b} \pm 0.00$	$0.13^{b} \pm 0.01$	$0.12^{b} \pm 0.00$	$0.13^{b} \pm 0.01$
C22:0	-	0.10 ± 0.00	0.08 ± 0.00	0.09 ± 0.00	0.09 ± 0.02	0.11 ± 0.02	0.11 ± 0.02
C20:4n6	$0.27^{a} \pm 0.07$	$0.05^{b} \pm 0.02$	$0.03^{b} \pm 0.01$	$0.02^{b} \pm 0.00$	$0.04^{b} \pm 0.02$	$0.02^{b} \pm 0.01$	$0.02^{b} \pm 0.00$
C23:0	-	0.01 ± 0.01	0.01 ± 0.01	0.02 ± 0.00	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.00
C24:0	-	0.06 ± 0.00	0.05 ± 0.01	0.06 ± 0.00	0.06 ± 0.01	0.07 ± 0.01	0.08 ± 0.01
C24:1	-	0.02 ± 0.00	-	-	-	0.01 ± 0.00	-
C22:6n3	-	-	-	0.03 ± 0.00	0.03 ± 0.01	0.04 ± 0.00	0.04 ± 0.00
SFA	$25.28^{a} \pm 0.23$	$40.68^{b} \pm 0.09$	$42.37^{bc} \pm 0.13$	$43.09^{c} \pm 0.20$	$43.20^{c} \pm 0.67$	$42.89^{c} \pm 0.55$	$41.84^{bc} \pm 0.59$

MUFA	$36.56^{a} \pm 0.11$	$44.29^{b} \pm 0.02$	$43.44^{b} \pm 0.08$	$43.37^{b} \pm 0.15$	$43.22^{b} \pm 0.50$	$43.34^{b} \pm 0.42$	$43.99^{b} \pm 0.55$
PUFA	$38.16^{a} \pm 0.15$	$15.03^{b} \pm 0.11$	$14.19^{c} \pm 0.05$	$13.55^{d} \pm 0.05$	$13.58^{d} \pm 0.16$	$13.77^{cd} \pm 0.14$	$14.17^{c} \pm 0.04$
UFA	$74.72^{a} \pm 0.23$	$59.32^{b} \pm 0.09$	$57.63^{bc} \pm 0.13$	$56.91^{c} \pm 0.20$	$56.80^{c} \pm 0.67$	$57.11^{c} \pm 0.55$	$58.16^{bc} \pm 0.59$
ΣTRANS	-	$0.14^{a} \pm 0.01$	$0.25^{b} \pm 0.01$	$0.28^{bc} \pm 0.01$	$0.31^{c} \pm 0.03$	$0.40^{d} \pm 0.01$	$0.36^{d} \pm 0.00$
C18:2 n6c/C16:0	$1.91^{a} \pm 0.02$	$0.42^{b} \pm 0.00$	$0.38^{c} \pm 0.00$	$0.36^{c} \pm 0.00$	$0.36^{c} \pm 0.01$	$0.37^{c} \pm 0.01$	$0.38^{bc} \pm 0.00$
MUFA/SFA	$1.45^{a} \pm 0.02$	$1.09^{b} \pm 0.00$	$1.03^{bc} \pm 0.01$	$1.01^{c} \pm 0.01$	$1.00^{c} \pm 0.03$	$1.01^{c} \pm 0.02$	$1.05^{bc} \pm 0.03$
PUFA/SFA	$1.51^{a} \pm 0.02$	$0.37^{b} \pm 0.00$	$0.33^{bc} \pm 0.00$	$0.31^{c} \pm 0.00$	$0.31^{c} \pm 0.01$	$0.32^{c} \pm 0.01$	$0.34^{bc} \pm 0.01$
UFA/SFA	$2.96^{a} \pm 0.04$	$1.46^{b} \pm 0.01$	$1.36^{bc} \pm 0.01$	$1.32^{c} \pm 0.01$	$1.31^{c} \pm 0.04$	$1.33^{c} \pm 0.03$	$1.39^{bc} \pm 0.03$

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.8- Fatty acid composition (%) of thermo-oxidized olive oil at different treatment times.

	THERMO-OXIDIZED OLIVE OIL						
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	$0.10^{a} \pm 0.08$	$0.14^{ab} \pm 0.00$	$0.24^{bc} \pm 0.08$	$0.29^{c} \pm 0.00$	$0.29^{c} \pm 0.00$	$0.43^{d} \pm 0.00$
C10:0	-	-	-	-	-	-	0.08 ± 0.07
C12:0	-	0.07 ± 0.06	-	0.07 ± 0.06	0.04 ± 0.06	-	0.15 ± 0.06
C14:0	$0.10^{a} \pm 0.00$	$0.10^{a} \pm 0.00$	$0.10^{a} \pm 0.00$	$0.10^{a} \pm 0.00$	$0.10^{a} \pm 0.00$	$0.10^{a} \pm 0.00$	$0.41^{b} \pm 0.20$
C15:0	-	-	-	-	-	-	0.04 ± 0.06
C16:0	$11.36^{a} \pm 0.50$	$12.49^{b} \pm 0.07$	$12.83^{bc} \pm 0.05$	$13.33^{cd} \pm 0.23$	$13.90^{de} \pm 0.09$	$14.06^{e} \pm 0.04$	$15.05^{f} \pm 0.39$
C16:1	$1.41^{a} \pm 0.06$	$1.69^{b} \pm 0.18$	$1.55^{ab} \pm 0.12$	$1.70^{b} \pm 0.00$	$1.71^{b} \pm 0.00$	$1.68^{b} \pm 0.06$	$1.71^{b} \pm 0.00$
C17:0	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C17:1	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C18:0	$2.62^{abc} \pm 0.00$	$2.25^{d} \pm 0.05$	$2.43^{cd} \pm 0.00$	$2.50^{bc} \pm 0.06$	$2.68^{ab} \pm 0.06$	$2.72^{a} \pm 0.05$	$3.09^{e} \pm 0.16$
C18:1 n9t	-	-	-	-	-	-	-
C18:1 n9c	$71.09^{ab} \pm 0.53$	$70.28^{b} \pm 0.58$	$71.29^{ab} \pm 0.26$	$71.48^{ab} \pm 0.21$	$71.54^{ab} \pm 0.12$	$71.97^{a} \pm 0.17$	$71.02^{ab} \pm 0.81$
C18:2 n6t	-	$0.15^{a} \pm 0.06$	$0.11^{a} \pm 0.00$	$0.07^{ab} \pm 0.06$	$0.11^{a} \pm 0.00$	$0.11^{a} \pm 0.00$	$0.11^{a} \pm 0.00$
C18:2 n6c	$12.00^{a} \pm 0.04$	$11.73^{b} \pm 0.19$	$10.63^{c} \pm 0.13$	$9.63^{d} \pm 0.05$	$8.85^{e} \pm 0.00$	$8.27^{f} \pm 0.04$	$7.29^{g} \pm 0.05$
C18:3 n3	$0.60^{a} \pm 0.00$	$0.48^{ab} \pm 0.21$	$0.36^{abc} \pm 0.00$	$0.32^{bc} \pm 0.07$	$0.28^{bc} \pm 0.07$	$0.24^{bc} \pm 0.00$	$0.20^{c} \pm 0.07$
C20:1	$0.48^{a} \pm 0.00$	$0.16^{b} \pm 0.06$	$0.19^{b} \pm 0.00$	$0.19^{b} \pm 0.00$	$0.23^{b} \pm 0.06$	$0.20^{b} \pm 0.00$	$0.19^{b} \pm 0.00$
C21:0	-	$0.28^{a} \pm 0.00$	$0.14^{b} \pm 0.00$	$0.14^{b} \pm 0.00$	$0.05^{c} \pm 0.08$	$0.14^{b} \pm 0.00$	-
C20:4 n6	0.11 ± 0.00	-	-	-	-	-	-
SFA	$14.19^{a} \pm 0.50$	$15.40^{b} \pm 0.20$	$15.75^{b} \pm 0.05$	$16.49^{bc} \pm 0.31$	$17.21^{c} \pm 0.09$	$17.53^{c} \pm 0.06$	$19.35^{d} \pm 0.92$
MUFA	$73.09^{ab} \pm 0.46$	$72.24^{b} \pm 0.49$	$73.15^{ab} \pm 0.18$	$73.48^{a} \pm 0.21$	$73.59^{a} \pm 0.09$	$73.95^{a} \pm 0.11$	$73.04^{ab} \pm 0.81$
PUFA	$12.71^{a} \pm 0.04$	$12.36^{a} \pm 0.29$	$11.10^{b} \pm 0.13$	$10.03^{c} \pm 0.10$	$9.24^{d} \pm 0.07$	$8.63^{e} \pm 0.04$	$7.61^{f} \pm 0.11$
UFA	$85.81^{a} \pm 0.50$	$84.60^{b} \pm 0.20$	$84.25^{b} \pm 0.05$	$83.51^{bc} \pm 0.31$	$82.83^{c} \pm 0.09$	$82.58^{c} \pm 0.09$	$80.65^{d} \pm 0.92$
ΣTRANS	-	0.15 ± 0.06	0.11 ± 0.00	0.07 ± 0.06	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C18:2 n6c/C16:0	$1.06^{a} \pm 0.05$	$0.94^{b} \pm 0.01$	$0.83^{c} \pm 0.01$	$0.72^{d} \pm 0.01$	$0.64^{e} \pm 0.00$	$0.59^{e} \pm 0.00$	$0.48^{f} \pm 0.02$
MUFA/SFA	$5.15^{a} \pm 0.21$	$4.69^{b} \pm 0.09$	$4.65^{b} \pm 0.03$	$4.46^{bc} \pm 0.10$	$4.28^{c} \pm 0.03$	$4.22^{c} \pm 0.02$	$3.78^{d} \pm 0.22$

PUFA/SFA	$0.90^{a} \pm 0.03$	$0.80^{b} \pm 0.01$	$0.70^{c} \pm 0.01$	$0.61^{d} \pm 0.02$	$0.54^{e} \pm 0.00$	$0.49^{e} \pm 0.00$	$0.39^{f} \pm 0.02$
UFA/SFA	$6.05^{a} \pm 0.24$	$5.49^{b} \pm 0.09$	$5.35^{bc} \pm 0.02$	$5.06^{cd} \pm 0.11$	$4.81^{d} \pm 0.03$	$4.71^{d} \pm 0.02$	$4.17^{e} \pm 0.24$

a-g: Different letters indicate significant differences ($p \leq 0{,}05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.9- Fatty acid composition (%) of frying olive oil at different treatment times.

	FRYING OLIVE OIL						
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	$0.14^{ab} \pm 0.14$	$0.05^{b} \pm 0.08$	$0.14^{ab} \pm 0.00$	$0.05^{b} \pm 0.08$	$0.48^{ab} \pm 0.44$	$0.62^{a} \pm 0.22$
C12:0	-	-	-	-	0.04 ± 0.06	-	-
C14:0	$0.10^{a} \pm 0.00$	$0.13^{ab} \pm 0.06$	$0.10^{a} \pm 0.00$	$0.20^{ab} \pm 0.00$	$0.17^{ab} \pm 0.06$	$0.24^{b} \pm 0.06$	$0.20^{ab} \pm 0.00$
C15:0	-	-	-	0.04 ± 0.06	-	-	0.07 ± 0.06
C16:0	$11.36^{a} \pm 0.50$	$12.16^{ab} \pm 0.28$	$12.94^{bc} \pm 0.05$	$13.80^{cd} \pm 0.14$	$14.18^{d} \pm 0.47$	$14.28^{d} \pm 0.12$	$14.52^{d} \pm 0.39$
C16:1	1.41 ± 0.06	1.48 ± 0.11	1.45 ±0.06	1.45 ± 0.06	1.43 ± 0.07	1.35 ± 0.07	1.35 ± 0.06
C17:0	0.11 ± 0.00	0.11 ± 0.00	0.04 ± 0.06	0.11 ± 0.00	0.11 ± 0.00	0.07 ± 0.06	0.11 ± 0.00
C17:1	0.11 ± 0.00	0.15 ± 0.06	0.07 ± 0.06	0.11 ± 0.00	0.19 ± 0.13	0.11 ± 0.00	0.15 ± 0.06
C18:0	$2.62^{a} \pm 0.00$	$2.73^{ab} \pm 0.01$	$2.80^{b} \pm 0.06$	$3.31^{d} \pm 0.06$	$3.03^{c} \pm 0.07$	$3.20^{d} \pm 0.05$	$3.21^{d} \pm 0.04$
C18:1 n9c	$71.09^{a} \pm 0.53$	$69.85^{b} \pm 0.44$	$69.66^{b} \pm 0.12$	$67.93^{c} \pm 0.31$	$67.48^{c} \pm 0.40$	$67.03^{cd} \pm 0.38$	$66.07^{d} \pm 0.42$
C18:2 n6t	-	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C18:2 n6c	$12.00^{a} \pm 0.04$	$12.14^{b} \pm 0.03$	$12.07^{ab} \pm 0.05$	$12.05^{ab} \pm 0.05$	$12.31^{c} \pm 0.06$	$12.55^{d} \pm 0.04$	$12.93^{e} \pm 0.04$
C18:3 n3	$0.60^{a} \pm 0.00$	$0.56^{a} \pm 0.07$	$0.36^{b} \pm 0.00$	$0.36^{b} \pm 0.00$	$0.36^{b} \pm 0.00$	$0.32^{b} \pm 0.07$	$0.24^{b} \pm 0.21$
C20:1	$0.48^{a} \pm 0.00$	$0.32^{b} \pm 0.11$	$0.19^{bc} \pm 0.19$	$0.16^{c} \pm 0.06$	$0.20^{bc} \pm 0.00$	$0.13^{c} \pm 0.06$	$0.19b^{c} \pm 0.00$
C20:2	-	-	0.04 ± 0.06	0.11 ± 0.00	0.07 ± 0.06	-	-
C20:4 n6	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C22:0	-	-	-	-	0.13 ± 0.23	-	-
C20:3 n6	-	-	-	-	0.04 ± 0.06	-	-
SFA	$14.19^{a} \pm 0.50$	$15.27^{b} \pm 0.23$	$15.93^{b} \pm 0.12$	$17.61^{c} \pm 0.16$	$17.57^{c} \pm 0.45$	$18.27^{cd} \pm 0.42$	$18.74^{d} \pm 0.37$
MUFA	$73.09^{a} \pm 0.46$	$71.81^{b} \pm 0.27$	$71.38^{b} \pm 0.09$	$69.65^{c} \pm 0.21$	$69.29^{cd} \pm 0.31$	$68.63^{de} \pm 0.39$	$67.76^{e} \pm 0.34$
PUFA	$12.71^{ab} \pm 0.04$	$12.92^{bc} \pm 0.10$	$12.69^{a} \pm 0.10$	$12.74^{ab} \pm 0.05$	$12.97^{c} \pm 0.11$	$13.10^{c} \pm 0.04$	$13.50^{d} \pm 0.07$
UFA	$85.81^{a} \pm 0.50$	$84.73^{b} \pm 0.23$	$84.07^{b} \pm 0.12$	$82.39^{c} \pm 0.16$	$82.26^{c} \pm 0.40$	$81.73^{cd} \pm 0.42$	$81.26^{c} \pm 0.37$
ΣTRANS	-	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00
C18:2 n6c/C16:0	$1.06^{a} \pm 0.05$	$1.00^{ab} \pm 0.02$	$0.93^{bc} \pm 0.01$	$0.87^{c} \pm 0.01$	$0.87^{c} \pm 0.03$	$0.88^{c} \pm 0.01$	$0.89^{c} \pm 0.02$
MUFA/SFA	$5.15^{a} \pm 0.21$	$4.70^{b} \pm 0.09$	$4.48^{b} \pm 0.04$	$3.95^{c} \pm 0.05$	$3.94^{c} \pm 0.11$	$3.76^{cd} \pm 0.11$	$3.62^{d} \pm 0.09$

PUFA/SFA	$0.90^{a} \pm 0.03$	$0.85^{ab} \pm 0.01$	$0.80^{b} \pm 0.01$	$0.72^{c} \pm 0.00$	$0.74^{c} \pm 0.03$	$0.72^{c} \pm 0.02$	$0.72^{c} \pm 0.02$
UFA/SFA	$6.05^{a} \pm 0.24$	$5.55^{b} \pm 0.10$	$5.28^{b} \pm 0.05$	$4.68^{c} \pm 0.05$	$4.68^{c} \pm 0.14$	$4.47^{c} \pm 0.13$	$4.34^{c} \pm 0.11$

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.10- Fatty acid composition (%) of olive oil extracted from French fries at different treatment times.

	OLIVE OIL EXTRACTED FROM FRENCH FRIES						
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	0.05 ± 0.08	0.10 ± 0.17	-	0.05 ± 0.08	-	-
C10:0	-	0.08 ± 0.13	-	-	-	-	-
C11:0	-	0.08 ± 0.13	-	-	-	-	-
C12:0	0.19 ± 0.06	0.18 ± 0.13	-	-	-	0.04 ± 0.06	0.04 ± 0.06
C14:0	0.97^{a} ± 0.16	0.72^{a} ± 0.20	0.20^{b} ± 0.00	0.20^{b} ± 0.00	0.17^{b} ± 0.06	0.20^{b} ± 0.00	0.24^{b} ± 0.06
C15:0	-	0.18 ± 0.22	0.04 ± 0.06	-	-	-	0.04 ± 0.06
C16:0	19.89^{a} ± 0.17	13.09^{b} ± 0.22	13.89^{b} ± 0.55	13.86^{b} ± 0.09	13.77^{b} ± 0.16	14.34^{b} ± 0.52	15.35^{b} ± 2.04
C16:1	0.11^{a} ± 0.19	2.04^{b}± 0.44	1.35^{c} ± 0.06	1.28^{c} ± 0.00	1.24^{c} ± 0.06	1.21^{c} ± 0.06	1.24^{c} ± 0.23
C17:0	-	-	0.11^{a} ± 0.00	0.11^{a} ± 0.00	0.04^{b} ± 0.06	0.11^{a} ± 0.00	0.11^{a} ± 0.00
C17:1	-	-	0.15 ± 0.06	0.11 ± 0.00	0.11 ± 0.00	0.11 ± 0.00	0.07 ± 0.06
C18:0	3.83^{a} ± 0.18	2.53^{b} ± 0.33	3.19^{c} ± 0.11	3.18^{cd} ± 0.06	3.01^{d} ± 0.06	3.45^{ac} ± 0.01	3.26^{cd} ± 0.08
C18:1 n9c	36.45^{a} ± 0.08	66.57^{b} ± 1.11	65.79^{bc} ± 0.60	65.65^{bc} ± 0.14	66.12^{b} ± 0.39	64.88^{bc} ± 0.55	63.31^{c} ± 1.91
C18:2 n6t	-	-	0.11 ± 0.00	0.11 ± 0.00	0.07 ± 0.06	0.11 ± 0.00	0.11 ± 0.11
C18:2 n6c	37.90^{a} ± 0.11	13.86^{b} ± 0.09	14.27^{bc} ± 0.36	14.67^{c} ± 0.01	14.69^{c} ± 0.16	14.86^{c} ± 0.09	15.53^{d} ± 0.46
C18:3 n3	0.41 ± 0.07	0.49 ± 0.12	0.48 ± 0.00	0.44 ± 0.14	0.40 ± 0.07	0.36 ± 0.00	0.36 ± 0.00
C20:1	-	0.07 ± 0.11	0.13 ± 0.06	0.10 ± 0.00	0.10 ± 0.00	0.10 ± 0.00	0.13 ± 0.06
C20:2	-	-	0.07 ± 0.06	0.11 ± 0.00	0.07 ± 0.06	0.07 ± 0.06	0.11 ± 0.00
C20:4 n6	0.27^{a} ± 0.07	0.08^{b} ± 0.13	0.11^{ab} ± 0.00	0.19^{ab} ± 0.06	0.11^{ab} ± 0.00	0.15^{ab} ± 0.06	0.11^{ab} ± 0.00
C22:1n9	-	-	-	-	0.04 ± 0.06	-	-
SFA	24.87^{a} ± 0.23	16.82^{b} ± 0.93	17.53^{b} ± 0.53	17.35^{b} ± 0.08	17.04^{b} ± 0.35	18.15^{b} ± 0.58	19.02^{b} ± 2.14
MUFA	36.56^{a} ± 0.11	68.68^{b} ± 0.86	67.42^{bc} ± 0.55	67.13^{bc} ± 0.14	67.57^{bc} ± 0.35	66.30^{cd} ± 0.49	64.75^{d} ± 1.69
PUFA	38.57^{a} ± 0.15	14.42^{b} ± 0.12	15.05^{bc} ± 0.35	15.51^{cd} ± 0.07	15.35^{c} ± 0.24	15.55^{cd} ± 0.19	16.22^{d} ± 0.45
UFA	75.13^{a} ± 0.23	83.10^{b} ± 0.98	82.47^{b} ± 0.53	82.65^{b} ± 0.08	82.92^{b} ± 0.28	81.85^{b} ± 0.58	80.98^{b} ± 2.14
ΣTRANS	-	-	0.11 ± 0.00	0.11 ± 0.00	0.07 ± 0.06	0.11 ± 0.00	0.11 ± 0.00
C18:2 n6c/C16:0	1.91^{a} ± 0.02	1.06^{b} ± 0.02	1.03^{b} ± 0.05	1.06^{b} ± 0.01	1.07^{b} ± 0.02	1.04^{b} ± 0.04	1.03^{b} ± 0.16

MUFA/SFA	$1.47^{a} \pm 0.02$	$4.09^{b} \pm 0.29$	$3.85^{bc} \pm 0.14$	$3.87^{bc} \pm 0.02$	$3.97^{bc} \pm 0.10$	$3.66^{bc} \pm 0.14$	$3.44^{c} \pm 0.45$
PUFA/SFA	$1.55^{a} \pm 0.02$	$0.86^{b} \pm 0.06$	$0.86^{b} \pm 0.04$	$0.89^{b} \pm 0.00$	$0.90^{b} \pm 0.02$	$0.86^{b} \pm 0.04$	$0.86^{b} \pm 0.11$
UFA/SFA	$3.02^{a} \pm 0.04$	$4.95^{b} \pm 0.34$	$4.71^{b} \pm 0.17$	$4.76^{b} \pm 0.03$	$4.87^{b} \pm 0.12$	$4.51^{b} \pm 0.18$	$4.30^{b} \pm 0.56$

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.11- Fatty acid composition (%) of thermo-oxidized sunflower oil at different treatment times.

THERMO-OXIDIZED SUNFLOWER OIL							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	-	-	-	-	-	-
C11:0	-	0.07±0.13	-	-	-	0.04±0.06	-
C14:0	0.10±0.36	0.16±0.06	0.20±0.00	0.15±0.07	0.27±0.12	0.23±0.06	0.20±0.00
C15:0	-	0.10±0.00	0.10±0.00	0.05±0.07	0.14±0.06	0.10±0.00	0.10±0.00
C16:0	5.53±0.78	5.87±0.22	6.75±0.74	6.43±0.18	8.59±3.00	7.78±0.71	7.15±0.09
C16:1	0.10±0.06	0.10±0.00	0.14±0.06	0.10±0.00	0.24±0.06	0.21±0.00	0.17±0.06
C17:0	-	0.07±0.06	0.11±0.00	0.05±0.08	0.11±0.00	0.11±0.00	0.11±0.00
C17:1	0.05±0.06	-	0.04±0.06	-	-	0.07±0.06	-
C18:0	3.10^{a}±0.50	3.22^{ab}±0.11	3.37^{ab}±0.09	3.62^{b}±0.06	3.58^{b}±0.23	3.78^{b}±0.10	3.94^{b}±0.09
C18:1 n9t	-	0.04^{a}±0.07	0.04^{a}±0.07	0.06^{a}±0.08	0.27^{ab}±0.07	0.27^{ab}±0.07	0.31^{b}±0.07
C18:1 n9c	31.62^{a}±3.02	32.29^{ab}±0.18	33.04^{ab}±0.29	34.20^{ab}±0.36	33.98^{b}±1.36	35.18^{b}±0.35	36.08^{b}±0.15
C18:2 n6t	0.32±0.06	0.36±0.06	0.11±0.00	0.11±0.00	0.26±0.17	0.29±0.13	0.29±0.13
C18:2 n6c	58.49±4.49	56.98±0.52	54.90±0.41	53.98±0.18	51.17±1.88	50.61±0.35	50.32±0.42
C18:3 n3	-	-	0.10±0.00	0.21±0.00	0.14±0.06	0.10±0.10	0.21±0.00
C20:0	0.12±0.07	0.12±0.00	0.12±0.00	0.06±0.08	0.04±0.07	0.08±0.14	-
C20:1	-	-	-	-	-	0.06±0.11	-
C20:2	0.10±0.06	0.10±0.00	0.17±0.06	0.10±0.15	0.21±0.00	0.14±0.12	0.21±0.00
C20:4 n6	0.47±0.23	0.47±0.00	0.51±0.06	0.62±0.07	0.73±0.21	0.67±0.00	0.64±0.05
C24:0	-	0.04^{a}±0.06	0.11^{b}±0.00	0.11^{bcd}±0.00	0.07^{bc}±0.06	0.11^{cd}±0.00	0.11^{d}±0.00
C24:1 n9	-	-	0.08±0.00	0.04±0.06	0.06±0.05	0.06±0.05	0.08±0.00
C22:6 n3	0.11±0.00	0.11±0.00	0.11±0.00	0.11±0.00	0.15±0.06	0.11±0.00	0.07±0.06
SFA	8.84±0.06	9.66±0.49	10.76±0.67	10.47±0.26	12.80±2.85	12.23±0.46	11.61±0.17
MUFA	31.77±0.13	32.31±0.09	33.34±0.10	34.40±0.20	34.55±0.10	35.85±0.08	36.64±0.15
PUFA	59.49±0.21	58.02±0.18	55.90±0.30	55.13±0.28	52.65±0.25	51.92±0.12	51.74±0.10
UFA	91.26±0.06	90.45±0.49	89.24±0.73	89.53±0.41	87.20±2.85	87.77±0.34	88.39±0.17

ΣTRANS	0.32±0.00	0.40±0.13	0.15±0.07	0.17±0.08	0.53±0.24	0.56±0.19	0.60±0.06
C18:2 n6c/C16:0	10.57±0.11	9.70±0.26	8.13±0.16	8.39±0.15	5.95±0.12	6.50±0.15	7.04±0.12
MUFA/SFA	3.59±0.21	3.34±0.19	3.10±0.08	3.28±0.11	2.70±0.09	2.93±0.08	3.15±0.09
PUFA/SFA	6.73±0.13	6.01±0.16	5.19±0.12	5.26±0.08	4.11±0.12	4.24±0.14	4.46±0.15
UFA/SFA	10.32±0.15	9.36±0.11	8.29±0.21	8.55±0.17	6.81±0.15	7.17±0.023	7.61±0.22

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.12- Fatty acid composition (%) of frying sunflower oil at different treatment times.

FRYING SUNFLOWER OIL							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	0.09^{a}±0.10	0.13^{ab}±0.09	0.14^{ab}±0.01	0.19^{ab}±0.10	0.20^{b}±0.10	0.22^{b}±0.10
C12:0	-	-	-	0.01±0.00	-	0.02±0.00	-
C14:0	0.10±0.36	0.08±0.01	0.08±0.01	0.10±0.01	0.08±0.01	0.12±0.10	0.12±0.09
C15:0	-	0.02±0.00	-	0.02±0.01	-	0.02±0.01	-
C16:0	5.53±0.78	6.20±0.37	7.31±0.40	7.13±0.53	7.59±0.48	7.81±1.05	8.47±0.97
C16:1	0.10±0.06	0.13±0.01	0.13±0.02	0.14±0.06	0.10±0.05	0.14±0.063	0.11±0.07
C17:0	-	0.04±0.02	0.03±0.01	0.04±0.02	0.04±0.03	0.04±0.01	0.03±0.02
C17:1	0.05±0.06	0.01±0.00	0.02±0.00	0.01±0.02	0.01±0.03	0.01±0.00	-
C18:0	3.10±0.50	3.47±0.05	3.60±0.04	3.66±0.42	3.06±0.36	3.81±0.37	3.84±0.45
C18:1n9t	-	0.08±0.054	0.08±0.06	0.14±0.10	0.08±0.09	0.17±0.10	0.22±0.10
C18:1n9c	31.51±3.02	32.68±0.95	31.20±1.63	33.58±0.23	33.65±0.22	34.18±0.10	32.61±0.09
C18:2 n6t	0.32^{a}±0.06	0.02^{b}±0.01	0.03^{b}±0.02	0.04^{b}±0.03	0.02^{b}±0.02	0.04^{b}±0.00	-
C18:2 n6c	58.49±4.49	56.82±1.05	56.90±0.95	54.77±0.90	54.91±1.27	53.22±0.60	54.12±0.54
C20:0	0.12^{ab}±00.07	0.01^{b}±0.00	0.29^{c}±0.01	-	0.22^{ac}±0.07	-	0.25^{c}±0.18
C20:1	-	0.02±0.01	0.11±0.00	0.09±0.01	0.05±0.00	0.09±0.01	-
C18:3 n3	-	0.03±0.02	0.06±0.01	0.04±0.00	-	0.05±0.00	-
C20:2	0.10±0.06	-	-	-	-	-	-
C20:4 n6	0.47±0.23	-	-	-	-	-	-
C20:3 n6	-	-	-	0.01±0.00	-	0.01±0..01	-
C20:3 n3	-	0.04±0.01	-	0.04±0.02	-	0.05±0.02	-
C23:0	-	0.23±0.01	-	-	-	-	-
C22:6 n3	0.11±0.00	-	-	-	-	-	-
C24:1 n9	-	0.03±0.02	-	0.02±0.00	-	0.03±0.01	-
SFA	8.84±0.06	10.13±0.12	11.45±0.15	11.11±0.16	11.18±0.20	12.01±0.28	12.94±0.31
MUFA	31.77±0.13	32.96±0.30	31.55±0.23	33.99±0.25	33.89±0.21	34.62±0.27	32.94±0.30

PUFA	59.49±0.21	56.91±0.25	57.00±0.16	54.91±0.10	54.93±0.15	53.37±0.18	54.12±0.21
UFA	91.26±0.06	89.87±0.21	88.55±0.19	88.89±0.20	88.82±0.15	87.99±0.19	87.06±0.25
ΣTRANS	0.32±0.00	0.10±0.06	0.12±0.10	0.19±0.04	0.10±0.08	0.21±0.12	0.22±0.13
C18:2 n6c/C16:0	10.58±0.11	9.16±0.14	7.78±0.13	7.68±0.11	7.23±0.21	6.81±0.16	6.38±0.15
MUFA/SFA	3.59±0.21	3.25±0.08	2.75±0.09	3.06±0.03	3.03±0.09	2.88±0.05	2.55±0.03
PUFA/SFA	6.73±0.13	5.62±0.31	4.98±0.10	4.94±0.05	4.91±0.16	4.44±0.09	4.18±0.02
UFA/SFA	10.32±0.15	8.87±0.12	7.73±0.16	8.00±0.06	7.94±0.12	7.33±0.11	6.73±0.14

a-b: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.13- Fatty acid composition (%) of sunflower oil extracted from French fries at different treatment times.

SUNFLOWER OIL EXTRACTED FROM FRENCH FRIES							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	0.09±0.10	0.14±0.10	0.14±0.10	0.27±0.19	0.19±0.10	0.14±0.05
C12:0	0.19^{a}±0.06	0.01^{b}±0.00	-	0.02^{b}±0.01	-	0.02^{b}±0.01	-
C14:0	0.97^{a}±0.16	0.11^{b}±0.01	0.10^{b}±0.02	0.16^{b}±0.02	0.23^{b}±0.03	0.17^{b}±0.04	0.15^{b}±0.03
C15:0	-	0.02±0.01	0.02±0.01	0.02±0.00	-	0.02±0.01	0.02±0.01
C16:0	19.89^{a}±0.17	7.42^{b}±0.38	8.06^{bc}±0.43	8.58^{bc}±0.23	10.48^{d}±0.13	9.21^{cd}±0.85	9.24^{cd}±0.71
C16:1	0.11±0.19	0.13±0.02	0.14±0.01	0.14±0.01	0.15±0.02	0.14±0.01	0.12±0.00
C17:0	-	0.04±0.04	0.04±0.03	0.04±0.01	0.05±0.01	0.04±0.02	0.04±0.03
C17:1	-	-	0.03±0.02	0.01±0.00	-	0.01±0.01	0.02±0.02
C18:0	3.83±0.18	3.58±0.21	3.62±0.12	3.75±0.07	3.52±0.09	3.86±0.220	3.92±0.02
C18:1n9t	-	0.09±0.12	0.21±0.15	0.15±0.01	0.12±0.00	0.18±0.15	0.16±0.11
C18:1n9c	36.45^{a}±0.08	32.96^{b}±0.85	33.33^{b}±0.94	33.74^{bc}±0.05	33.05^{b}±0.04	34.12^{bc}±0.41	34.47^{c}±0.38
C18:2 n6t	-	0.03±0.01	0.02±0.02	0.04±0.02	0.04±0.03	0.04±0.01	0.04±0.03
C18:2 n6c	37.90^{a}±0.11	55.40^{b}±0.98	53.74^{c}±1.18	52.92^{cd}±0.62	51.63^{de}±0.51	51.70^{de}±0.40	51.10^{e}±0.34
C20:0	-	-	0.31±0.05	-	0.28±0.07	-	0.35±0.09
C20:1	-	-	0.10±0.00	0.15±0.02	0.08±0.01	0.17±0.05	0.12±0.08
C18:3 n3	0.41±0.07	0.03±0.01	0.10±0.07	0.04±0.01	0.12±0.00	0.04±0.02	0.12±0.07
C20:4 n6	0.27±0.07	-	-	-	-	-	-
C20:3 n3	-	0.05±0.02	-	0.05±0.00	-	0.05±0.03	-
C23:0	-	-	0.02±0.02	-	-	-	-
C24:1 n9	-	0.03±0.00	0.01±0.00	0.03±0.01	-	0.03±0.01	-
SFA	25.27±0.23	11.28±0.32	12.31±0.27	12.72±0.12	14.82±0.40	13.52±0.20	13.86±0.15
MUFA	36.56±0.11	33.21±0.31	33.82±0.25	34.22±0.26	33.40±0.19	34.64±0.21	34.89±0.24
PUFA	38.17±0.15	55.51±0.25	53.87±0.23	53.06±0.32	51.78±0.16	51.84±0.17	51.25±0.21
UFA	74.73±0.23	88.72±0.40	87.69±0.32	87.28±0.18	85.18±0.30	86.48±0.27	86.14±0.30
ΣTRANS	-	0.12±0.01	0.23±0.10	0.20±0.12	0.15±0.06	0.22±0.10	0.19±0.13

C18:2 n6c/C16:0	1.91±0.02	7.47±0.53	6.68±0.47	6.16±0.44	4.93±0.35	5.61±0.40	5.53±0.39
MUFA/SFA	1.47±0.02	2.94±0.21	2.75±0.20	2.70±0.19	2.25±0.16	2.56±0.18	2.52±0.18
PUFA/SFA	1.55±0.02	4.92±0.35	4.38±0.45	4.17±0.30	2.25±0.16	2.56±0.18	2.52±0.18
UFA/SFA	3.02±0.04	7.87±0.56	7.12±0.50	6.90±0.49	5.75±0.41	6.40±0.45	6.22±0.44

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.14- Fatty acid composition (%) of thermo-oxidized lard at different treatment times.

THERMO-OXIDIZED LARD							
	Time(h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	-	-	0.10±0.09	0.15±0.00	0.15±0.00	0.15±0.00
C10:0	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00
C12:0	0.45^{a}±0.00	0.11^{b}±0.00	0.11^{b}±0.00	0.11^{b}±0.00	0.11^{b}±0.00	0.11^{b}±0.00	0.11^{b}±0.00
C14:0	1.60±0.06	1.50±0.06	1.56±0.00	1.50±0.12	1.64±0.06	1.61±0.06	1.64±0.06
C15:0	0.11±0.00	0.11±0.00	0.11±0.00	0.11±0.00	0.11±0.00	0.11±0.00	0.11±0.00
C16:0	21.46^{ac}±0.04	20.84^{b}±0.11	21.30^{bc}±0.14	21.32^{bc}±0.35	21.82^{acd}±0.16	21.89^{ad}±0.12	22.15^{d}±0.22
C16:1	2.01^{a}±0.06	2.19^{b}±0.01	2.22^{b}±0.06	2.26^{bc}±0.07	2.38^{c}±0.07	2.28^{bc}±0.06	2.31^{bc}±0.00
C17:0	0.31±0.07	0.35±0.00	0.34±0.00	0.34±0.00	0.35±0.00	0.35±0.00	0.35±0.00
C17:1	0.23^{a}±0.00	0.31^{b}±0.07	0.23^{a}±0.00	0.23^{a}±0.00	0.35^{b}±0.00	0.35^{b}±0.00	0.35^{b}±0.00
C18:0	14.73^{a}±0.03	14.04^{b}±0.12	14.11^{b}±0.06	14.18^{b}±0.04	14.47^{c}±0.11	14.64^{ac}±0.11	14.80^{a}±0.13
C18:1 n9c	44.77^{a}±0.27	46.86^{b}±0.12	47.12^{b}±0.33	47.17^{b}±0.59	46.54^{b}±0.27	46.88^{b}±0.08	47.00^{b}±0.18
C18:2 n6t	0.11±0.00	-	-	-	-	-	-
C18:2 n6c	12.95^{a}±0.09	12.27^{b}±0.14	11.76^{c}±0.13	11.54^{c}±0.05	10.99^{d}±0.02	10.53^{e}±0.05	10.00^{f}±0.02
C20:0	0.46±0.07	-	-	-	-	-	-
C18:3 n3	-	0.55^{a}±0.00	0.47^{b}±0.06	0.44^{b}±0.00	0.44^{b}±0.00	0.44^{b}±0.00	0.33^{c}±0.00
C20:1	-	0.03±0.06	-	0.03±0.06	-	-	-
C21:0	0.43±0.38	-	-	-	-	-	-
C20:2	0.15^{a}±0.25	0.47^{b}±0.06	0.44^{b}±0.00	0.44^{b}±0.00	0.44^{b}±0.00	0.44^{b}±0.00	0.48^{b}±0.06
C20:3 n6	0.11±0.00	0.12±0.00	-	-	-	-	0.08±0.07
C20:4 n6	-	0.13±0.12	0.10±0.00	0.10±0.00	0.10±0.00	0.10±0.00	0.03±0.06
SFA	39.66±0.41	37.07±0.23	37.65±0.09	37.79±0.54	38.77±0.21	38.98±0.07	39.42±0.16
MUFA	47.01±0.22	49.39±0.12	49.57±0.27	49.70±0.50	49.26±0.23	49.50±0.02	49.65±0.18
PUFA	13.33±0.34	13.54±0.14	12.77±0.19	12.51±0.05	11.97±0.02	11.51±0.05	10.92±0.05
UFA	60.34±0.41	62.93±0.23	62.35±0.09	62.21±0.54	61.23±0.21	61.02±0.07	60.58±0.16
TRANS	0.04±0.07	-	-	-	-	-	-

C18:2 n6C/C16:0	0.60±0.01	0.59±0.01	0.55±0.00	0.54±0.01	0.63±0.01	0.64±0.00	0.65±0.00
MUFA/SFA	1.19±0.01	1.33±0.01	1.32±0.00	1.32±0.01	0.50±0.00	0.48±0.01	0.45±0.01
PUFA/SFA	0.34±0.02	0.37±0.01	0.34±0.01	0.33±0.03	1.27±0.01	1.27±0.00	1.26±0.01
UFA/SFA	1.52±0.01	1.70±0.01	1.66±0.00	1.65±0.01	1.58±0.00	1.57±0.00	1.54±0.00

a-f: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.15- Fatty acid composition (%) of frying lard at different treatment times.

FRYING LARD							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	0.15±0.00	0.15±0.00	0.15±0.01	0.15±0.00	0.15±0.00	0.15±0.00
C10:0	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00	0.12±0.00
C12:0	0.45±0.00	0.45±0.00	0.41±0.07	0.46±0.02	0.41±0.06	0.45±0.00	0.41±0.06
C14:0	1.60±0.06	1.79±0.01	1.78±0.11	1.83±0.08	1.74±0.21	1.79±0.00	1.71±0.04
C15:0	0.11^{a}±0.00	0.11^{a}±0.00	0.04^{b}±0.06	0.11^{a}±0.00	0.11^{a}±0.00	0.11^{a}±0.00	0.11^{a}±0.00
C16:0	21.46^{a}±0.04	22.47^{b}±0.07	22.98^{bc}±0.34	23.58^{cd}±0.18	23.25^{cd}±0.40	23.72^{d}±0.18	23.49^{cd}±0.26
C16:1	2.01±0.06	2.16±0.05	2.09±0.11	2.30±0.46	2.01±0.06	1.99±0.00	1.86±0.03
C17:0	0.31±0.07	0.31±0.07	0.35±0.00	0.36±0.01	0.31±0.07	0.31±0.07	0.31±0.07
C17:1	0.23±0.00	0.27±0.07	0.23±0.00	0.24±0.01	0.23±0.00	0.23±0.00	0.23±0.00
C18:0	14.73±0.03	14.84±0.12	15.20±0.25	15.06±0.34	14.93±0.29	14.96±0.08	14.96±0.30
C18:1 n9t	-	0.20±0.07	0.08±0.14	0.25±0.01	0.20±0.18	0.37±0.00	0.12±0.21
C18:1 n9c	44.77^{a}±0.27	43.59^{ab}±0.21	43.73^{ab}±0.28	42.60^{b}±0.50	43.15^{b}±0.95	42.93^{b}±0.20	42.74^{b}±0.72
C18:2 n6t	0.11^{a}±0.00	0.27^{ab}±0.07	0.27^{ab}±0.07	0.24^{ab}±0.01	0.42^{b}±0.24	0.27^{ab}±0.07	0.23^{ab}±0.00
C18:2 n6c	12.95±0.09	12.28±0.11	11.93±0.04	11.88±0.06	11.91±0.19	11.99±0.12	12.92±1.32
C20:0	0.46^{a}±0.07	0.17^{b}±0.14	0.12^{b}±0.00	-	0.12^{b}±0.00	-	-
C18:3 n3	-	-	-	0.42^{a}±0.35	-	0.11^{b}±0.00	0.11^{b}±0.00
C20:1	-	0.20±0.35	-	-	0.40±0.35	0.03±0.06	0.07±0.06
C21:0	0.43±0.38	0.58±0.00	0.53±0.08	0.39±0.07	0.43±0.00	0.43±0.00	0.43±0.01
C20:2	0.15±0.25	-	-	-	-	-	-
C20:3 n6	0.11±0.00	0.04±0.07	-	-	0.08±0.07	0.04±0.07	0.04±0.07
C20:4 n6	-	-	-	-	0.03±0.06	-	-
SFA	39.66±0.41	40.98±0.14	41.67±0.11	42.07±0.41	41.57±0.51	42.04±0.17	41.68±0.57
MUFA	47.01±0.22	46.43±0.32	46.13±0.03	45.39±0.03	45.99±0.51	45.55±0.17	45.02±0.84
PUFA	13.33±0.34	12.59±0.18	12.20±0.09	12.54±0.42	12.44±0.18	12.41±0.15	13.29±1.38
UFA	60.34±0.41	59.02±0.14	58.33±0.11	57.93±0.41	58.43±0.51	57.96±0.17	58.32±0.57

TRANS	0.04±0.07	0.47±0.00	0.35±0.12	0.49±0.02	0.62±0.41	0.64±0.07	0.35±0.21
C18:2 n6cC16:0	0.60±0.01	0.69±0.00	0.71±0.00	0.73±0.01	0.71±0.02	0.73±0.01	0.71±0.02
MUFA/SFA	1.19±0.01	0.55±0.00	0.52±0.01	0.50±0.01	0.51±0.02	0.51±0.01	0.55±0.06
PUFA/SFA	0.34±0.02	1.13±0.01	1.11±0.00	1.08±0.01	1.11±0.03	1.08±0.01	1.08±0.01
UFA/SFA	1.52±0.01	1.44±0.00	1.40±0.00	1.38±0.01	1.41±0.01	1.38±0.00	1.40±0.04

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.16- Fatty acid composition (%) of lard extracted from French fries at different treatment times.

LARD EXTRACTED FROM FRENCH FRIES							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	-	-	0.05±0.08	0.15±0.00	0.15±0.00	0.15±0.15
C10:0	-	0.12±0.00	0.12±0.00	0.08±0.07	0.12±0.00	0.12±0.00	0.12±0.00
C12:0	0.17^{a}±0.08	0.34^{b}±0.00	0.34^{b}±0.00	0.26^{b}±0.14	0.41^{b}±0.07	0.38^{b}±0.06	0.41^{b}±0.07
C14:0	0.88^{a}±0.08	1.57^{b}±0.00	1.58^{b}±0.00	1.41^{bc}±0.39	1.75^{c}±0.06	1.68^{bc}±0.00	1.72^{c}±0.13
C15:0	-	0.11±0.00	0.11±0.00	0.07±0.06	0.11±0.00	0.11±0.00	0.11±0.00
C16:0	19.98^{a}±0.12	21.83^{b}±0.11	22.24^{b}±0.07	20.79^{b}±3.01	23.77^{c}±0.32	23.59^{c}±0.13	23.95^{c}±0.67
C16:1	0.16a±0.23	1.94^{b}±0.06	1.87^{b}±0.00	1.65^{b}±0.30	1.91^{b}±0.06	1.87^{b}±0.00	1.83^{b}±0.07
C17:0	-	0.31±0.07	0.35±0.00	0.34±0.02	0.27±0.07	0.27±0.07	0.23±0.00
C17:1	-	0.23±0.00	0.23±0.00	0.22±0.01	0.23±0.00	0.23±0.00	0.23±0.00
C18:0	3.93^{a}±0.02	14.52^{bc}±0.07	14.86^{b}±0.05	14.07^{b}±1.03	14.08^{cd}±0.07	13.97^{cd}±0.11	13.76^{d}±0.31
C18:1 n9t	-	0.04±0.07	0.20±0.07	0.16±0.14	0.20±0.19	0.28±0.07	0.41±0.07
C18:1 n9c	36.41^{a}±0.07	43.38^{b}±0.11	43.35^{b}±0.09	42.67^{b}±0.72	42.25^{c}±0.11	42.12^{cd}±0.12	41.90^{d}±0.29
C18:2 n6t	-	-	-	-	0.08^{a}±0.13	0.23^{b}±0.00	0.27^{b}±0.07
C18:2 n6c	37.87^{a}±0.15	14.58^{b}±0.06	13.84^{c}±0.13	17.74^{cd}±6.11	13.98^{c}±0.08	14.45^{bd}±0.06	14.31^{bcd}±0.15
C20:0	0.37^{a}±0.00	0.33^{ab}±0.07	0.25^{ab}±0.00	0.20^{ab}±0.08	0.17^{ab}±0.07	0.21^{ab}±0.07	0.17^{b}±0.07
C18:3 n3	-	-	-	-	-	-	-
C20:1	-	-	-	-	-	-	-
C21:0	-	0.58^{a}±0.00	0.58^{a}±0.00	0.29^{b}±0.25	0.53^{a}±0.17	0.29^{b}±0.00	0.34^{bc}±0.08
C20:2	-	-	-	-	-	-	-
C20:3 n6	-	0.12^{a}±0.00	0.08^{b}±0.07	-	-	-	-
C20:4 n6	0.23±0.00	-	-	-	-	0.07±0.06	0.10±0.00
SFA	25.33±0.23	39.71±0.07	40.42±0.04	37.56±4.95	41.36±0.27	40.75±0.10	40.95±0.27
MUFA	36.57±0.11	45.59±0.04	45.66±0.08	44.70±1.16	44.59±0.13	44.50±0.19	44.37±0.16
PUFA	38.10±0.15	14.70±0.06	13.92±0.06	17.74±6.11	14.05±0.21	14.75±0.10	14.68±0.11

UFA	74.67±0.23	60.29±0.07	59.58±0.04	62.44±4.95	58.64±0.27	59.25±0.10	59.05±0.27
TRANS	-	0.04±0.07	0.20±0.07	0.16±0.14	0.28±0.25	0.51±0.07	0.68±0.14
C18:2n6c/C16:0	1.90±0.02	0.66±0.00	0.68±0.00	0.61±0.12	0.71±0.01	0.69±0.00	0.69±0.01
MUFA/SFA	1.44±0.02	0.67±0.00	0.62±0.01	0.90±0.46	0.59±0.01	0.61±0.01	0.60±0.02
PUFA/SFA	1.50±0.02	1.15±0.00	1.13±0.00	1.20±0.14	1.08±0.01	1.09±0.01	1.08±0.01
UFA/SFA	2.95±0.04	1.52±0.00	1.47±0.00	1.66±0.25	1.42±0.01	1.45±0.00	1.44±0.00

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.17- Fatty acid composition (%) of thermo-oxidized mix oil at different treatment times.

THERMO-OXIDIZED MIX OIL							
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	0.03^{a}±0.01	0.05^{ab}±0.00	0.07^{b}±0.01	0.11^{c}±0.01	0.14^{d}±0.01	0.18^{e}±0.00
C14:0	0.05±0.01	0.04±0.01	0.05±0.00	0.05±0.00	0.04±0.00	0.05±0.00	0.06±0.01
C15:0	0.02±0.00	0.02±0.01	0.02±0.00	0.02±0.00	0.02±0.00	0.03±0.01	0.02±0.00
C16:0	4.99^{a}±0.04	4.99^{a}±0.06	4.99^{a}±0.05	5.17^{ab}±0.02	5.38^{bc}±0.09	5.44^{c}±0.02	5.60^{c}±0.08
C16:1	0.17±0.00	0.16±0.02	0.16±0.00	0.17±0.00	0.17±0.02	0.18±0.01	0.19±0.00
C17:0	0.05±0.00	0.05±0.00	0.06±0.00	0.05±0.00	0.05±0.00	0.05±0.01	0.05±0.01
C17:1	0.05±0.00	0.04±0.01	0.04±0.01	0.04±0.01	0.05±0.01	0.04±0.01	0.06±0.00
C18:0	2.41^{a}±0.01	2.43^{ab}±0.02	2.51^{bc}±0.02	2.54^{c}±0.00	2.56^{c}±0.05	2.69^{d}±0.01	2.74^{d}±0.02
C18: 1 n9t	0.02^{a}±0.01	0.09^{a}±0.01	0.29^{b}±0.08	0.24^{b}±0.00	0.28^{b}±0.03	0.44^{c}±0.01	0.53^{c}±0.02
C18:1 n9c	59.92^{a}±0.09	60.34^{ab}±0.04	60.77^{ab}±0.10	61.67^{bc}±0.03	62.28^{cd}±0.48	63.01^{cd}±0.13	63.54^{d}±0.74
C18:2 n6t	-	0.01^{a}±0.01	0.03^{ab}±0.02	0.02^{ab}±0.00	0.03^{ab}±0.01	0.07^{bc}±0.01	0.08^{c}±0.02
C18:2 n6c	25.70^{a}±0.01	25.12^{b}±0.04	24.63^{c}±0.03	23.86^{d}±0.00	22.90^{e}±0.06	22.06^{f}±0.01	21.07^{g}±0.15
C20:0	0.43^{a}±0.02	0.47^{ab}±0.03	0.47^{ab}±0.01	0.46^{ab}±0.00	0.50^{b}±0.04	0.51^{b}±0.04	0.50^{b}±0.01
C18:3 n6	0.16^{a}±0.00	0.22^{ab}±0.00	0.27^{bc}±0.00	0.32^{cd}±0.00	0.35^{de}±0.03	0.42^{e}±0.02	0.40^{e}±0.02
C20:1	0.74^{a}±0.04	0.91^{b}±0.05	0.80^{ab}±0.02	0.83^{ab}±0.00	0.81^{ab}±0.06	0.88^{ab}±0.01	0.87^{ab}±0.02
C18:3 n3	4.43a±0.00	4.04^{ab}±0.03	3.74^{abc}±0.01	$3.35a^{bc}$±0.02	3.04^{bc}±0.04	2.67^{c}±0.00	2.82^{c}±0.80
C21:0	-	-	0.02^{a}±0.01	0.01^{a}±0.00	0.06^{a}±0.01	0.08^{b}±0.04	0.04^{a}±0.03
C20:2	0.04±0.00	0.04±0.00	0.04±0.01	0.05±0.00	0.04±0.00	0.04±0.01	0.04±0.00
C22:0	0.42^{a}±0.04	0.49^{ab}±0.01	0.53^{ab}±0.01	0.51^{ab}±0.01	0.49^{ab}±0.06	0.56^{b}±0.02	0.56^{b}±0.03
C20:3 n6	0.01^{a}±0.00	0.02^{a}±0.00	0.02^{ab}±0.00	0.02^{ab}±0.00	0.02^{ab}±0.00	0.03^{b}±0.00	0.03^{b}±0.01
C22:1 n9	0.18±0.00	0.20±0.01	0.21±0.01	0.21±0.01	0.20±0.02	0.22±0.01	0.22±0.00
C23:0	0.02±0.00	0.02±0.00	0.02±0.00	0.03±0.01	0.03±0.01	0.03±0.01	0.03±0.00
C22:2	0.01±0.00	0.02±0.01	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00
C24:0	0.11^{a}±0.02	0.16^{ab}±0.00	0.17^{ab}±0.00	0.16^{ab}±0.00	0.15^{ab}±0.02	0.19^{b}±0.01	0.18^{b}±0.03

C24:1	0.05[a]±0.01	0.07[ab]±0.01	0.08[ab]±0.01	0.08[ab]±0.01	0.07[ab]±0.01	0.08[ab]±0.00	0.10[b]±0.01
C22:6 n3	0.01±0.02	0.03±0.01	0.03±0.01	0.05±0.00	0.34±0.40	0.07±0.00	0.09±0.01
SFA	8.49±0.04	8.70±0.05	8.87±0.05	9.06±0.01	9.39±0.01	9.77±0.07	9.96±0.00
MUFA	61.14±0.05	61.81±0.06	62.35±0.01	63.24±0.04	63.87±0.33	64.86±0.11	65.49±0.69
PUFA	30.36±0.00	29.50±0.00	28.78±0.06	27.69±0.03	26.74±0.34	25.38±0.04	24.55±0.69
UFA	91.51±0.04	91.30±0.05	91.13±0.05	90.94±0.01	90.61±0.01	90.23±0.07	90.04±0.00
ΣTRANS	0.02±0.00	0.10±0.03	0.32±0.11	0.26±0.08	0.31±0.13	0.51±0.16	0.61±0.09
C18:2 n6c/C16:0	5.15±0.04	5.04±0.05	4.94±0.05	4.61±0.02	4.26±0.06	4.05±0.02	3.77±0.02
MUFA/SFA	7.20±0.04	7.10±0.05	7.03±0.04	6.98±0.01	6.80±0.03	6.64±0.06	6.57±0.07
PUFA/SFA	3.57±0.02	3.39±0.02	3.24±0.02	3.06±0.00	2.85±0.04	2.60±0.02	2.46±0.07
UFA/SFA	10.77±0.06	10.50±0.07	10.27±0.06	10.03±0.01	9.65±0.02	9.24±0.08	9.04±0.00

a-g: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.18- Fatty acid composition (%) of frying mix oil at different treatment times.

	FRYING MIX OIL						
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0		0.05^{ab}±0.01	0.07^{b}±0.01	0.09^{bc}±0.00	0.14^{cd}±0.03	0.17^{d}±0.01	0.18^{d}±0.01
C14:0	0.05^{ab}±0.01	0.04^{a}±0.01	0.05^{ab}±0.00	0.05^{ab}±0.00	0.05^{ab}±0.01	0.06^{b}±0.00	0.06^{b}±0.00
C15:0	0.02±0.00	0.04±0.02	0.02±0.00	0.02±0.00	0.02±0.00	0.03±0.01	0.02±0.00
C16:0	4.99^{a}±0.04	5.06^{ab}±0.04	5.18^{ab}±0.06	5.31^{bc}±0.03	5.50^{cd}±0.17	5.58^{cd}±0.04	5.65^{d}±0.05
C16:1	0.17±0.00	0.19±0.02	0.18±0.01	0.17±0.00	0.18±0.01	0.18±0.00	0.18±0.00
C17:0	0.05±0.00	0.05±0.01	0.05±0.00	0.05±0.00	0.05±0.00	0.05±0.00	0.06±0.00
C17:1	0.05±0.00	-	-	-	0.04±0.01	0.05±0.00	0.05±0.00
C18:0	2.41^{ab}±0.01	2.36^{a}±0.20	2.53^{abc}±0.00	2.57^{abc}±0.01	2.61^{abc}±0.02	2.68^{bc}±0.02	2.77^{c}±0.01
C18: 1 n9t	0.02±0.01	0.07±0.01	0.12±0.01	0.18±0.01	0.22±0.01	0.24±0.02	0.15±0.19
C18:1 n9c	59.92^{ab}±0.09	59.60^{b}±0.68	60.43^{ab}±0.08	60.50^{ab}±0.05	60.68^{ab}±0.07	60.67^{ab}±0.12	60.99^{a}±0.15
C18:2 n6t	-	0.05±0.02	0.02±0.01	0.03±0.02	0.02±0.00	0.03±0.00	0.05±0.01
C18:2 n6c	25.70^{a}±0.01	25.51^{ab}±0.15	25.23^{bc}±0.02	25.14^{c}±0.02	25.15^{c}±0.08	25.05^{cd}±0.05	24.69^{d}±0.16
C20:0	0.43±0.02	0.58±0.17	0.44±0.01	0.45±0.00	0.41±0.04	0.41±0.00	0.43±0.01
C18:3 n6	0.16±0.00	0.44±0.30	0.28±0.01	0.31±0.01	0.28±0.00	0.30±0.00	0.32±0.01
C20:1	0.74±0.04	0.84±0.07	0.77±0.03	0.74±0.03	0.71±0.06	0.70±0.01	0.72±0.03
C18:3 n3	4.43^{a}±0.00	4.25^{a}±0.32	3.65^{b}±0.00	3.41^{bc}±0.01	3.05^{cd}±0.00	2.85^{d}±0.00	2.64^{d}±0.05
C21:0	-	0.02±0.02	0.05±0.01	0.05±0.01	0.01±0.01	0.03±0.02	0.03±0.03
C20:2	0.04±0.00	0.04±0.01	0.03±0.01	0.04±0.00	0.04±0.00	0.04±0.00	0.03±0.00
C22:0	0.42±0.04	0.42±0.08	0.45±0.06	0.45±0.02	0.41±0.06	0.43±0.01	0.46±0.03
C20:3 n6	0.01^{ab}±0.00	0.01^{a}±0.01	0.02^{bc}±0.00	0.02^{bc}±0.00	0.02^{bc}±0.00	0.03^{c}±0.00	0.03^{c}±0.00
C22:1 n9	0.18±0.00	0.17±0.04	0.18±0.02	0.18±0.01	0.16±0.01	0.16±0.00	0.17±0.01
C23:0	0.02±0.00	0.02±0.00	0.02±0.00	0.02±0.00	0.02±0.00	0.02±0.00	0.02±0.00
C22:2	0.01±0.00	0.01±0.01	0.01±0.00	0.02±0.01	0.01±0.00	0.02±0.01	0.01±0.00
C24:0	0.11±0.02	0.13±0.02	0.13±0.03	0.13±0.02	0.12±0.02	0.12±0.01	0.14±0.01
C24:1	0.05±0.01	0.06±0.01	0.07±0.01	0.06±0.00	0.05±0.01	0.06±0.00	0.07±0.01

C22:6 n3	0.01^{a}±0.02	0.02^{ab}±0.00	0.03^{ab}±0.01	0.04^{abc}±0.01	0.05^{bc}±0.00	0.06^{bc}±0.01	0.07^{c}±0.01
SFA	8.49±0.04	8.75±0.10	8.99±0.05	9.16±0.01	9.33±0.07	9.57±0.08	9.83±0.03
MUFA	61.14±0.05	60.92±0.65	61.74±0.03	61.83±0.03	62.04±0.15	62.05±0.11	62.33±0.08
PUFA	30.36±0.00	30.33±0.75	29.27±0.01	29.01±0.02	28.63±0.08	28.38±0.03	27.83±0.11
UFA	91.51±0.04	91.25±0.10	91.01±0.05	90.84±0.01	90.67±0.07	90.43±0.08	90.17±0.03
TRANS	0.02±0.00	0.12±0.03	0.14±0.02	0.21±0.05	0.24±0.06	0.27±0.04	0.20±0.07
C18:2 n6c/C16:0	5.15±0.04	5.04±0.01	4.87±0.06	4.74±0.03	4.57±0.13	4.49±0.02	4.37±0.01
MUFA/SFA	7.20±0.04	6.96±0.01	6.87±0.04	6.75±0.01	6.65±0.06	6.49±0.06	6.34±0.01
PUFA/SFA	3.57±0.02	3.47±0.13	3.26±0.02	3.16±0.00	3.07±0.01	2.97±0.02	2.83±0.02
UFA/SFA	10.77±0.06	10.42±0.13	10.13±0.06	9.91±0.01	9.72±0.08	9.45±0.09	9.17±0.03

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.19- Fatty acid composition (%) of mix oil extracted from French fries at different treatment times.

	MIX OIL EXTRACTED FROM FRENCH FRIES						
	Time (h)						
Fatty acids (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
C8:0	-	0.05^{a}±0.00	0.06^{ab}±0.02	0.11^{bc}±0.02	0.12^{c}±0.02	0.13^{c}±0.02	0.15^{c}±0.01
C12:0	0.17±0.08	-	-	-	-	-	-
C14:0	0.88^{a}±0.08	0.04^{b}±0.03	0.05^{b}±0.00	0.04^{b}±0.01	0.05^{b}±0.01	0.05^{b}±0.01	0.05^{b}±0.01
C15:0	-	0.02±0.00	0.03±0.01	0.03±0.00	0.02±0.00	0.03±0.01	0.03±0.01
C16:0	19.98^{a}±0.12	5.12^{b}±0.00	5.29^{bc}±0.11	5.34^{bc}±0.00	5.45^{c}±0.12	5.47^{c}±0.01	5.52^{c}±0.03
C16:1	0.16±0.23	0.21±0.07	0.16±0.01	0.19±0.02	0.17±0.02	0.17±0.00	0.16±0.00
C17:0	-	0.04^{a}±0.01	0.05^{ab}±0.00	0.08^{b}±0.02	0.07^{ab}±0.02	0.05^{ab}±0.01	0.06^{ab}±0.00
C17:1	-	0.06^{ab}±0.00	0.05^{ab}±0.01	0.04^{a}±0.01	0.04^{a}±0.00	0.04^{a}±0.01	0.06^{b}±0.01
C18:0	3.93^{a}±0.02	2.62^{b}±0.01	2.68^{bc}±0.01	2.67^{bc}±0.06	2.68^{bc}±0.14	2.83^{bc}±0.02	2.91^{c}±0.03
C18: 1 n9t	-	0.09^{a}±0.01	0.14^{ab}±0.01	0.18^{bc}±0.02	0.21^{cd}±0.03	0.25^{de}±0.00	0.30^{e}±0.00
C18:1 n9c	36.41^{a}±0.07	58.14^{b}±0.12	58.09^{b}±0.10	57.85^{b}±1.02	57.84^{b}±0.99	58.23^{b}±0.40	58.38^{b}±0.07
C18:2 n6t	-	0.02±0.00	0.03±0.01	0.12±0.08	0.18±0.17	0.05±0.01	0.06±0.00
C18:2 n6c	37.87^{a}±0.15	27.41^{b}±0.05	27.53^{b}±0.16	26.80^{c}±0.03	26.95^{c}±0.07	26.88^{c}±0.18	26.93^{c}±0.02
C20:0	0.37±0.00	0.46±0.01	0.45±0.04	0.69±0.23	0.71±0.32	0.47±0.00	0.50±0.00
C18:3 n6	-	0.21±0.01	0.27±0.01	0.45±0.17	0.45±0.20	0.31±0.02	0.32±0.01
C20:1	-	0.64±0.02	0.63±0.00	0.69±0.02	0.68±0.03	0.68±0.00	0.67±0.01
C18:3 n3	-	3.81^{a}±0.02	3.42^{ab}±0.00	3.52^{ab}±0.44	3.25^{ab}±0.32	3.13^{ab}±0.56	2.53^{b}±0.04
C21:0	-	0.04±0.01	0.05±0.02	0.06±0.02	0.09±0.04	0.06±0.01	0.05±0.03
C20:2	-	0.04±0.01	0.05±0.01	0.10±0.07	0.04±0.01	0.04±0.01	0.05±0.02
C22:0	-	0.51±0.02	0.51±0.11	0.52±0.03	0.52±0.06	0.59±0.02	0.64±0.05
C20:3 n6	-	0.01^{a}±0.00	0.03^{ab}±0.02	0.02^{ab}±0.00	0.02^{ab}±0.00	0.02^{ab}±0.00	0.04^{b}±0.02
C22:1 n9	-	0.19±0.01	0.17±0.04	0.17±0.01	0.16±0.01	0.18±0.01	0.19±0.03
C23:0	-	0.02±0.00	0.03±0.01	0.07±0.05	0.03±0.01	0.03±0.00	0.04±0.01
C24:0	-	0.15±0.01	0.14±0.04	0.15±0.01	0.17±0.02	0.17±0.01	0.20±0.01
C24:1	-	0.07±0.00	0.07±0.02	0.06±0.00	0.06±0.00	0.07±0.01	0.08±0.01

C22:6 n3	-	0.02^{a}±0.00	0.03^{ab}±0.01	0.04^{abc}±0.01	0.05^{bcd}±0.00	0.06^{cd}±0.00	0.07^{d}±0.01
C20:4 n6	0.23±0.00	-	-	-	-	-	-
SFA	25.33±0.23	9.07±0.08	9.32±0.13	9.75±0.24	9.90±0.27	9.87±0.02	10.14±0.07
MUFA	36.57±0.11	59.39±0.06	59.31±0.01	59.19±0.98	59.16±1.04	59.63±0.39	59.86±0.03
PUFA	38.10±0.15	31.54±0.02	31.37±0.11	31.06±0.74	30.94±0.77	30.49±0.42	30.00±0.03
UFA	74.67±0.23	90.93±0.08	90.68±0.13	90.25±0.24	90.10±0.27	90.13±0.02	89.86±0.07
ΣTRANS	-	0.11±0.02	0.17±0.07	0.30±0.10	0.39±0.06	0.30±0.11	0.36±0.09
C18:2 n6c/C16:0	1.90±0.02	5.35±0.01	5.20±0.08	5.02±0.00	4.94±0.10	4.91±0.02	4.88±0.03
MUFA/SFA	1.44±0.02	6.55±0.06	6.36±0.09	6.07±0.25	5.98±0.27	6.04±0.02	5.90±0.04
PUFA/SFA	1.50±0.02	3.48±0.03	3.37±0.06	3.19±0.00	3.13±0.01	3.09±0.05	2.96±0.02
UFA/SFA	2.95±0.04	10.02±0.09	9.73±0.15	9.26±0.25	9.10±0.27	9.13±0.03	8.86±0.06

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.20- Trend of C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, Σtrans and UFA/SFA and their correlation index R^2 with TPC in bi-fractionated palm oil samples at different thermal treatment (thermo-oxidation, frying and extraction from French fries).

	thermo-oxidized bi-fractionated palm oil					frying bi-fractionated palm oil					bi-fractionated palm oil extracted from French fries				
	C8:0	C18:2	C18:2/C16	Σtrans	UFA/SFA	C8	C18:2	C18:2/C16	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA
0	0.02	12.50	0.35	0.06	1.41	0.02	12.5	0.35	0.06	1.41	-	37.9	1.91	-	2.96
8	0.04	11.64	0.32	0.17	1.38	0.05	12.07	0.34	0.14	1.41	0.06	14.73	0.42	0.14	1.46
16	0.09	10.63	0.28	0.23	1.31	0.08	11.6	0.32	0.22	1.37	0.10	13.93	0.38	0.25	1.36
24	0.12	9.93	0.26	0.32	1.27	0.12	11.29	0.31	0.29	1.34	0.12	13.29	0.36	0.28	1.32
32	0.14	9.25	0.24	0.42	1.26	0.18	10.75	0.27	0.30	1.18	0.15	13.3	0.36	0.31	1.31
40	0.16	8.67	0.22	0.50	1.23	0.16	11.17	0.30	0.38	1.29	0.15	13.5	0.37	0.40	1.33
48	0.20	8.09	0.21	0.57	1.19	0.15	11.36	0.31	0.43	1.32	0.16	13.9	0.38	0.36	1.39
R^2	0.9134	0.9593	0.9715	0.942	0.9213	0.893	0.8233	0.678	0.9523	0.5204	0.9405	0.7124	0.6988	0.9363	0.7338

Tab. 3.21- Trend of C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, Σtrans and UFA/SFA and their correlation index R^2 with TPC in olive oil samples at different thermal treatment (thermo-oxidation, frying and extraction from French fries).

	thermo-oxidized olive oil					frying olive oil					olive oil extracted from French fries				
	C8:0	C18:2	C18:2/C16	Σtrans	UFA/SFA	C8	C18:2	C18:2/C16	Σtrans	UFA/SFA	C8	C18:2	C18:2/C16	Σtrans	UFA/SFA
0	-	12	1.06	-	6.05	-	12.00	1.06	-	6.05	-	37.9	1.91	-	3.02
8	0.10	11.73	0.94	0.15	5.49	0.14	12.14	1.00	0.11	5.55	0.05	13.86	1.06	-	4.95
16	0.14	10.63	0.83	0.11	5.35	0.05	12.07	0.93	0.11	5.28	0.10	14.27	1.03	0.11	4.71
24	0.24	9.63	0.72	0.07	5.06	0.14	12.05	0.87	0.11	4.68	-	14.67	1.06	0.11	4.76
32	0.29	8.85	0.64	0.11	4.81	0.05	12.31	0.87	0.11	4.68	0.05	14.69	1.07	0.07	4.87
40	0.29	8.27	0.59	0.11	4.71	0.48	12.55	0.88	0.11	4.47	-	14.86	1.04	0.11	4.51
48	0.43	7.29	0.48	0.11	4.17	0.62	12.93	0.89	0.11	4.34	-	15.53	1.03	0.11	4.3
R^2	0.897	0.9487	0.9461	0.1815	0.9045	0.6989	0.6889	0.7176	-	0.9264	0.0178	0.8297*	0.5316	0.4479	0.7468*

*correlation doesn' t include values at time 0.

Tab. 3.22- Trend of C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, Σtrans and UFA/SFA and their correlation index R^2 with TPC in sunflower oil samples at different thermal treatment (thermo-oxidation, frying and extraction from French fries).

	thermo-oxidized sunflower oil					frying sunflower oil					sunflower oil extracted from French fries				
	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA
0	-	58.49	10.57	0.32	10.32		58.49	10.58	0.32	10.32	-	37.90	1.91	-	3.02
8	-	56.98	9.07	0.40	9.36	0.09	56.82	9.16	0.10	8.87	0.09	55.40	7.47	0.12	7.87
16	-	54.90	8.13	0.15	8.29	0.13	56.9	7.78	0.12	7.73	0.14	53.74	6.68	0.23	7.12
24	-	53.98	8.39	0.17	8.55	0.14	54.77	7.68	0.19	8.00	0.14	52.92	6.16	0.20	6.09
32	-	51.17	5.95	0.53	6.81	0.19	54.91	7.23	0.10	7.94	0.27	51.63	4.93	0.15	5.75
40	-	50.61	6.05	0.56	7.17	0.2	53.22	6.81	0.21	7.33	0.19	51.70	5.61	0.22	6.04
48	-	50.32	7.04	0.60	7.61	0.22	54.12	6.38	0.22	6.73	0.14	51.10	5.53	0.19	6.22
R^2		0.9302	0.8388	0.3142	0.8476	0.8629	0.7776	0.9885	0.135	0.9392	0.5578	0.9287*	0.9155*	0.0585	0.8201*

* correlation doesn' t include values at time 0.

Tab. 3.23- Trend of C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, Σtrans and UFA/SFA and their correlation index R^2 with TPC in lard samples at different thermal treatment (thermo-oxidation, frying and extraction from French fries).

	thermo-oxidized lard					frying lard					lard extracted from French fries				
	C8:0	C18:2	C18:2/C16	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA
0	-	12.95	0.60	0.04	1.52	-	12.95	0.60	0.04	1.52	-	37.87	1.90	-	2.95
8	-	12.27	0.59	-	1.70	0.15	12.28	0.69	0.47	1.44	-	14.58	0.66	0.04	1.52
16	-	11.76	0.55	-	1.66	0.15	11.93	0.71	0.35	1.40	-	13.84	0.68	0.20	1.47
24	0.10	11.54	0.54	-	1.65	0.15	11.88	0.73	0.49	1.38	0.05	17.74	0.61	0.16	1.66
32	0.15	10.99	0.63	-	1.58	0.15	11.91	0.71	0.62	1.41	0.15	13.98	0.71	0.28	1.42
40	0.15	10.53	0.64	-	1.57	0.15	11.99	0.73	0.64	1.38	0.15	14.45	0.69	0.51	1.45
48	0.15	10.00	0.65	-	1.54	0.15	12.92	0.71	0.35	1.40	0.15	14.31	0.69	0.68	1.44
R^2	-	0.9428	0.6773*	-	0.9349*	-	0.2909	0.5232	0.4622	0.5299	-	0.7782	0.7446	0.9531*	0.8137

* correlation doesn' t include values at time 0.

Tab. 3.24- Trend of C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, Σtrans and UFA/SFA and their correlation index R^2 with TPC in mix oil samples at different thermal treatment (thermo-oxidation, frying and extraction from French fries).

	thermo-oxidized mix oil					frying mix oil					mix oil extracted from French fries				
	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA	C8:0	C18:2	C18:2/C16:0	Σtrans	UFA/SFA
0	-	25.70	5.15	0.02	10.77	-	25.70	5.15	0.02	10.77	-	37.87	1.90	-	2.95
8	0.03	25.12	5.04	0.10	10.50	0.05	25.51	5.04	0.12	10.42	0.05	27.41	5.35	0.11	10.02
16	0.05	24.63	4.94	0.32	10.27	0.07	25.23	4.87	0.14	10.13	0.06	27.53	5.20	0.17	9.73
24	0.07	23.86	4.61	0.26	10.03	0.09	25.14	4.74	0.21	9.91	0.11	26.8	5.02	0.30	9.26
32	0.11	22.90	4.26	0.31	9.65	0.14	25.15	4.57	0.24	9.72	0.12	26.95	4.94	0.39	9.10
40	0.14	22.06	4.05	0.51	9.24	0.17	25.05	4.49	0.27	9.45	0.13	26.88	4.91	0.30	9.13
48	0.18	21.07	3.77	0.61	9.04	0.18	24.69	4.37	0.20	9.17	0.15	26.93	4.88	0.36	8.86
R^2	0.885	0.8797	0.8512	0.8184	0.8284	0.9406	0.8885	0.9838	0.6779	0.9662	0.9209	0.4016	0.2348	0.7933	0.2162
R^2*	0.8868	0.8682	0.8225	0.8096	0.8114	0.9542	0.8722	0.9936	0.6111	0.9932	0.9209	0.5089	0.858	0.6852	0.8888

* correlation doesn' t include values at time 0.

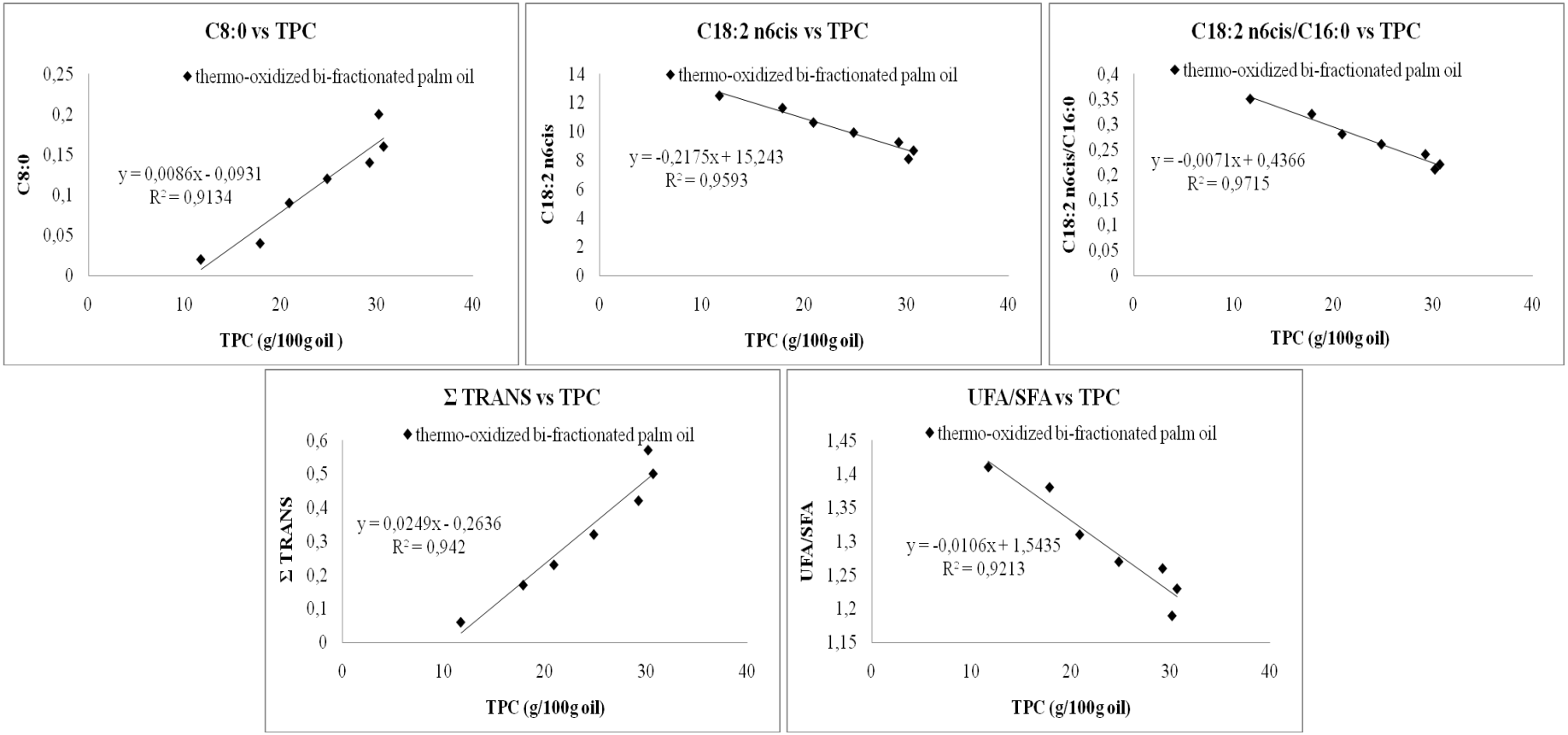

Fig. 3.2-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, ΣTRANS and UFA/SFA in thermo-oxidized bi-fractionated palm oil samples.

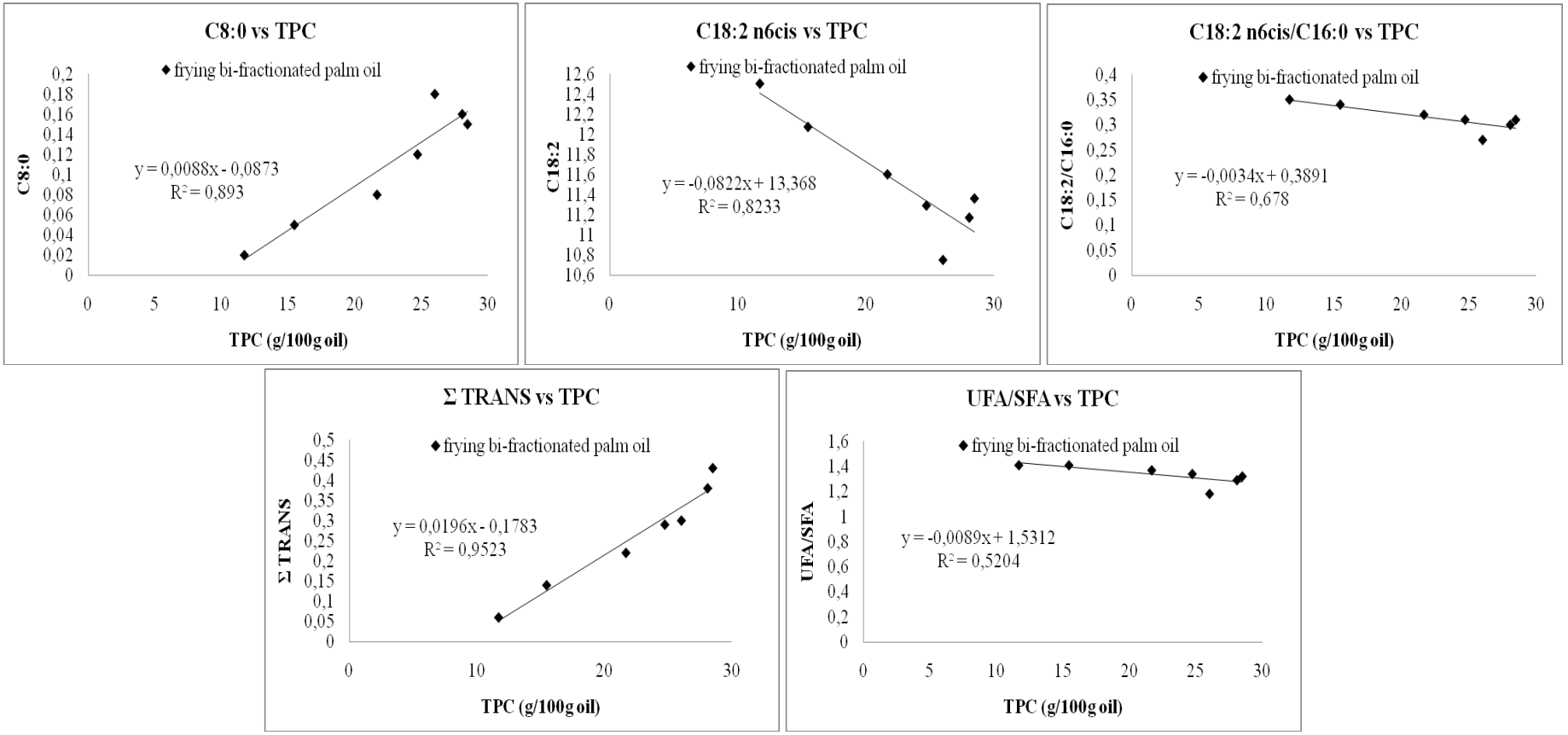

Fig. 3.3-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, ΣTRANS and UFA/SFA in frying bi-fractionated palm oil samples.

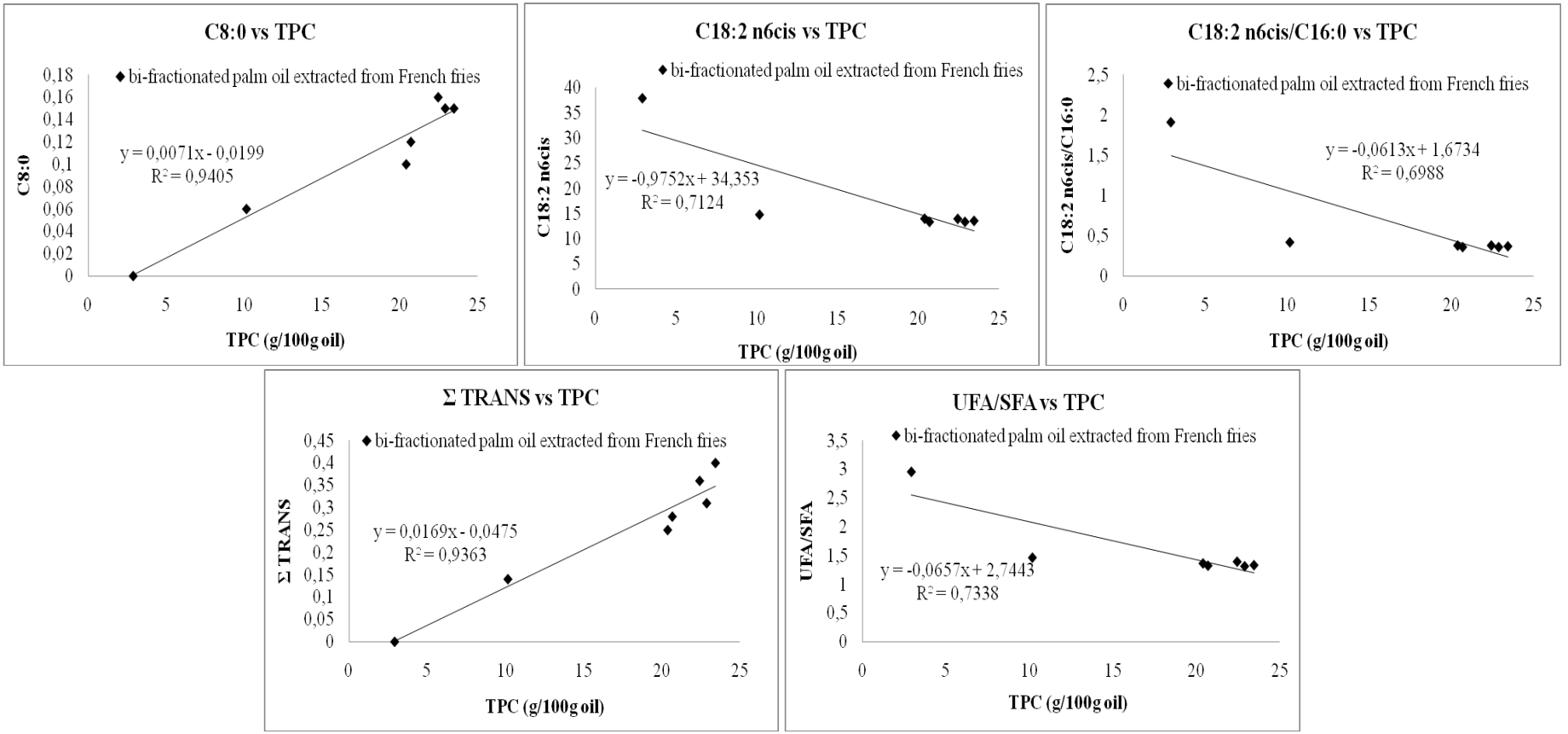

Fig. 3.4-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/C16:0, ΣTRANS and UFA/SFA in bi-fractionated palm oil extracted from French fries.

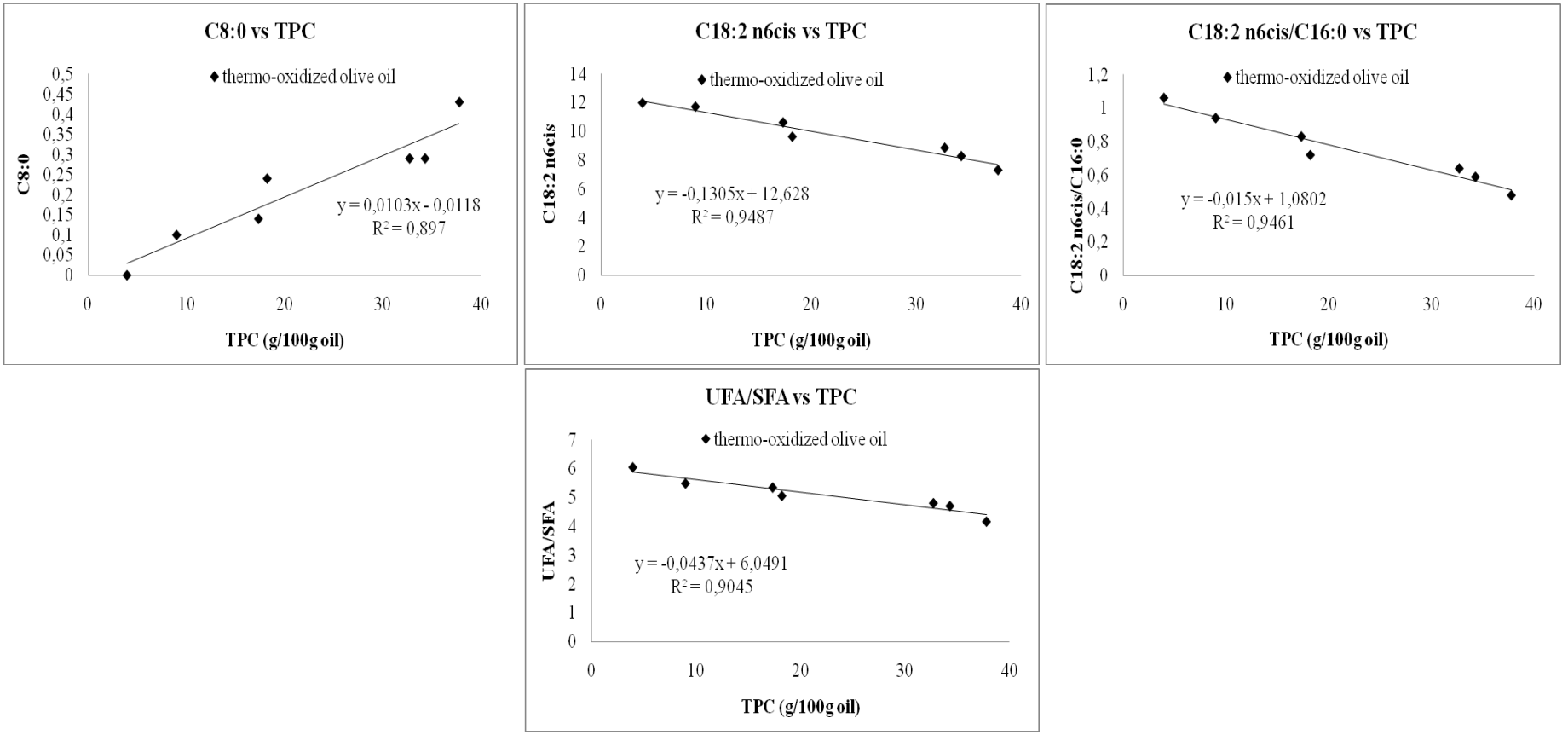

Fig. 3.5-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/C16:0 andUFA/SFA in thermo-oxidized olive oil samples.

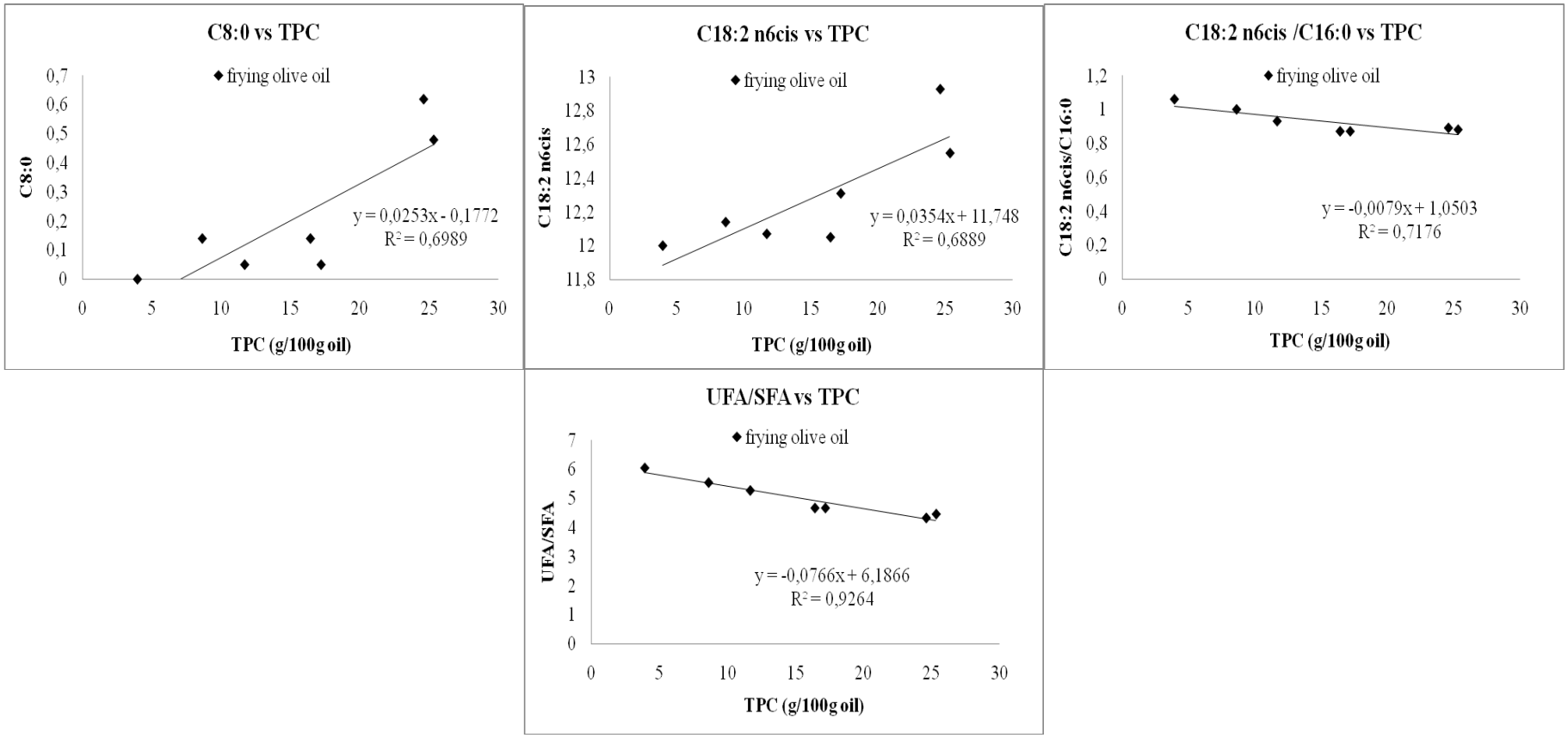

Fig. 3.6-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/C16:0 and UFA/SFA in frying olive oil.

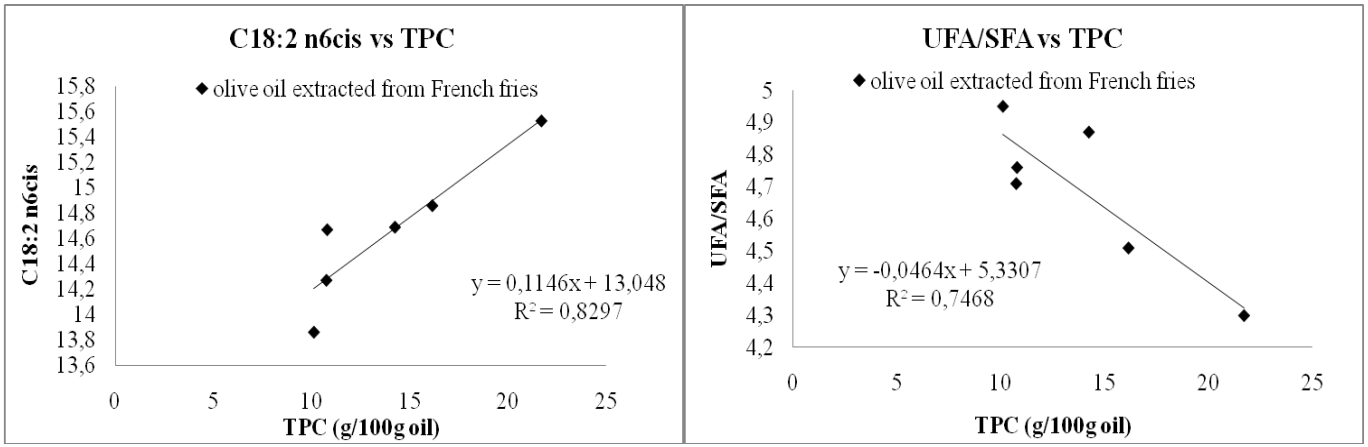

Fig. 3.7-Correlations between TPC and C18:2 n6cis and UFA/SFA in olive oil samples extracted from French fries (without values at time 0).

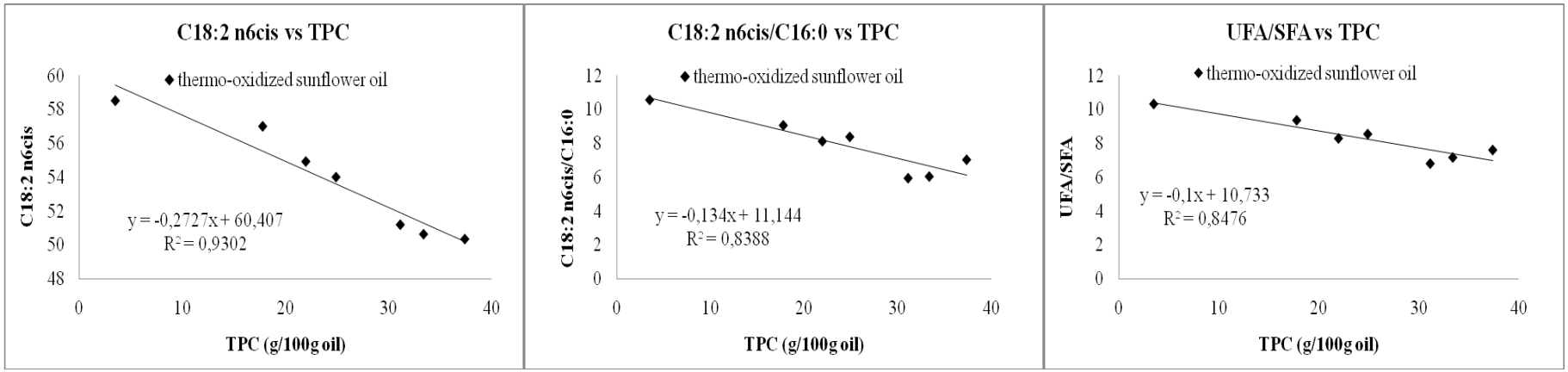

Fig. 3.8-Correlations between TPC and C18:2 n6cis, C18:2 n6cis/C16:0, and UFA/SFA in thermo-oxidized sunflower oil samples.

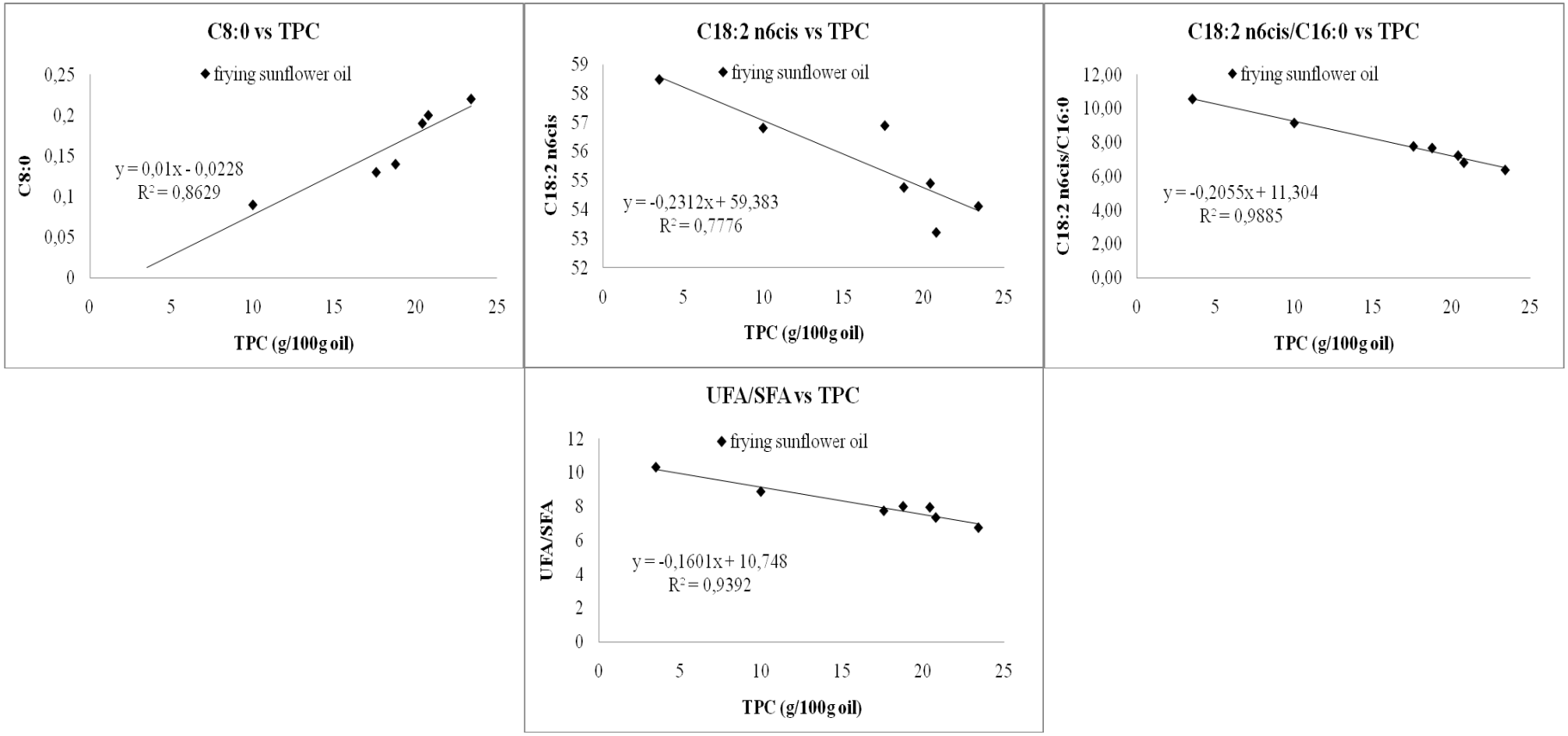

Fig. 3.9-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/C16:0 and UFA/SFA in frying sunflower oil samples.

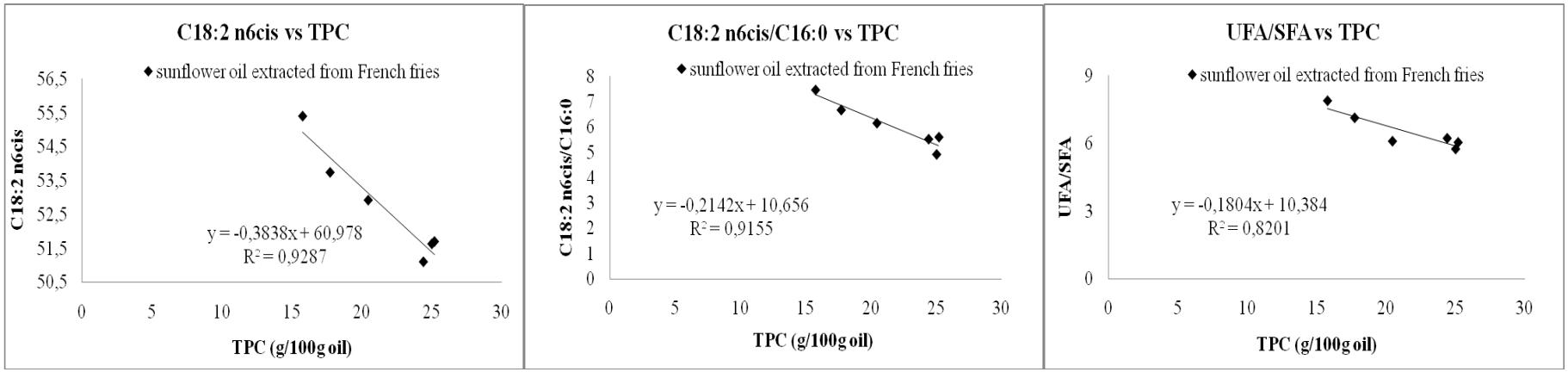

Fig. 3.10-Correlations between TPC and C18:2 n6cis, C18:2 n6cis/C16:0 and UFA/SFA in sunflower oil samples extracted from French fries without values at time 0.

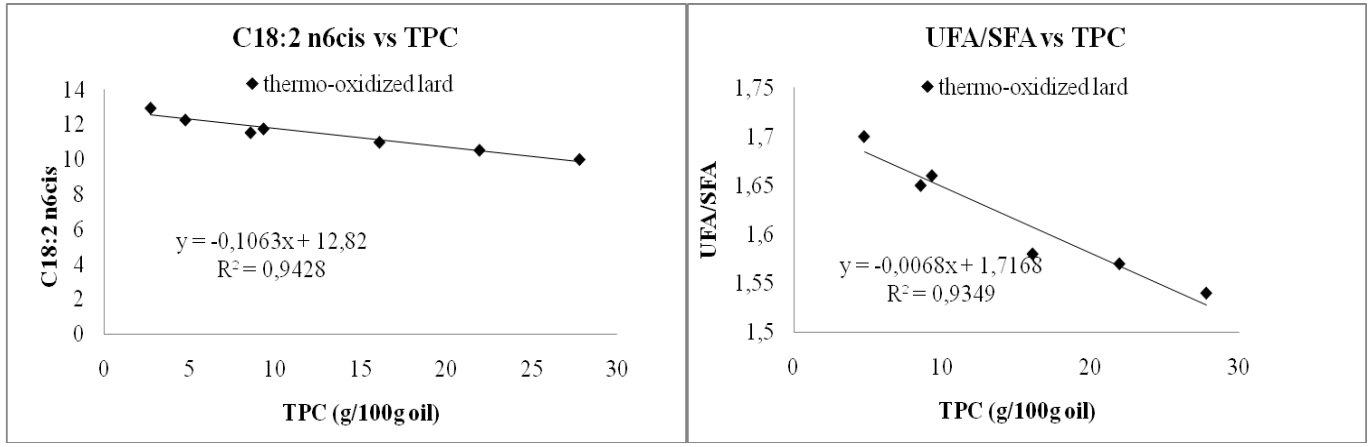

Fig. 3.11-Correlations between TPC and C18:2 n6cis and UFA/SFA (without value at time 0) in thermo-oxidized lard samples.

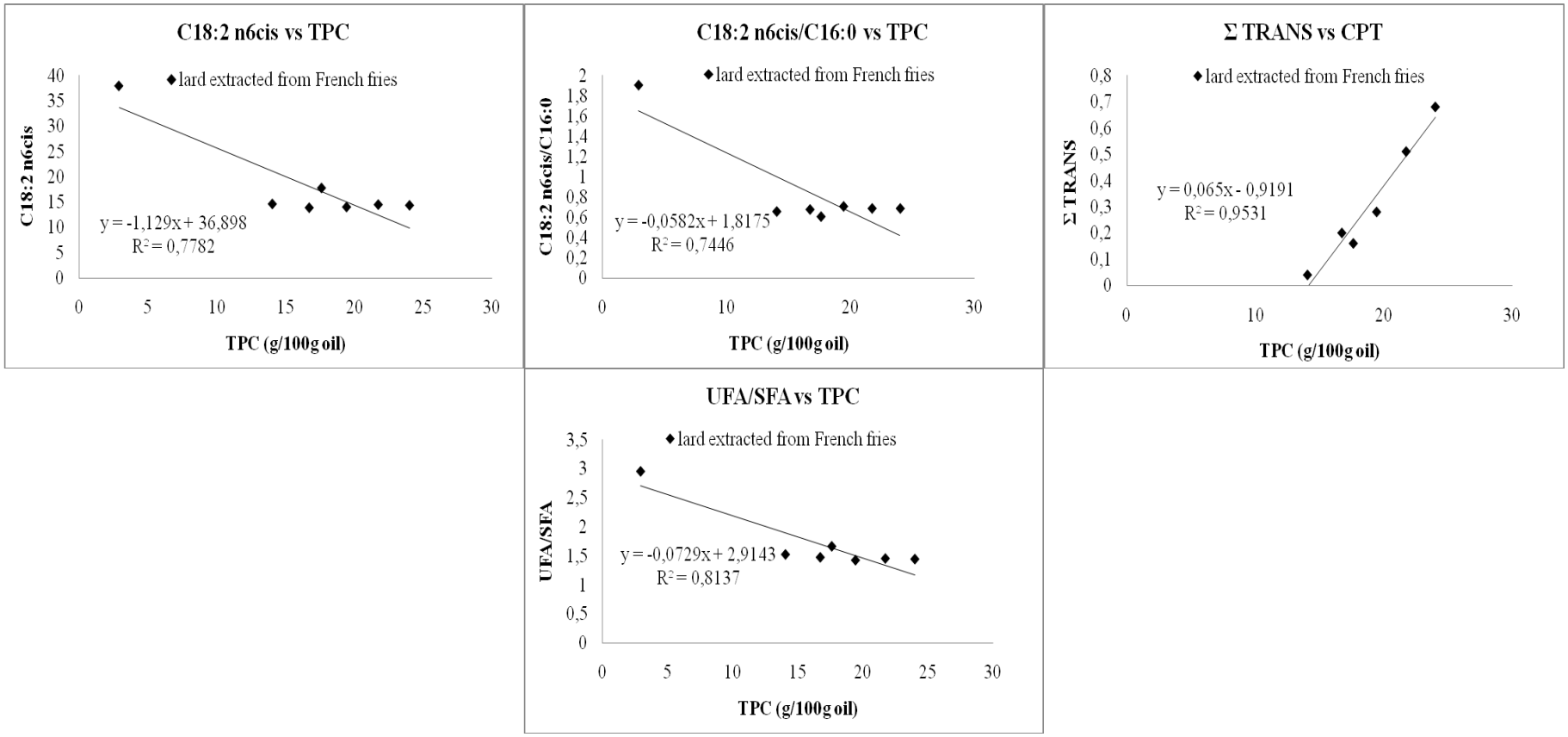

Fig. 3.12-Correlations between TPC and C18:2 n6cis, C18:2 n6cis/c16:0, Σtrans (without value at time 0) and UFA/SFA in lard samples extracted from French fries.

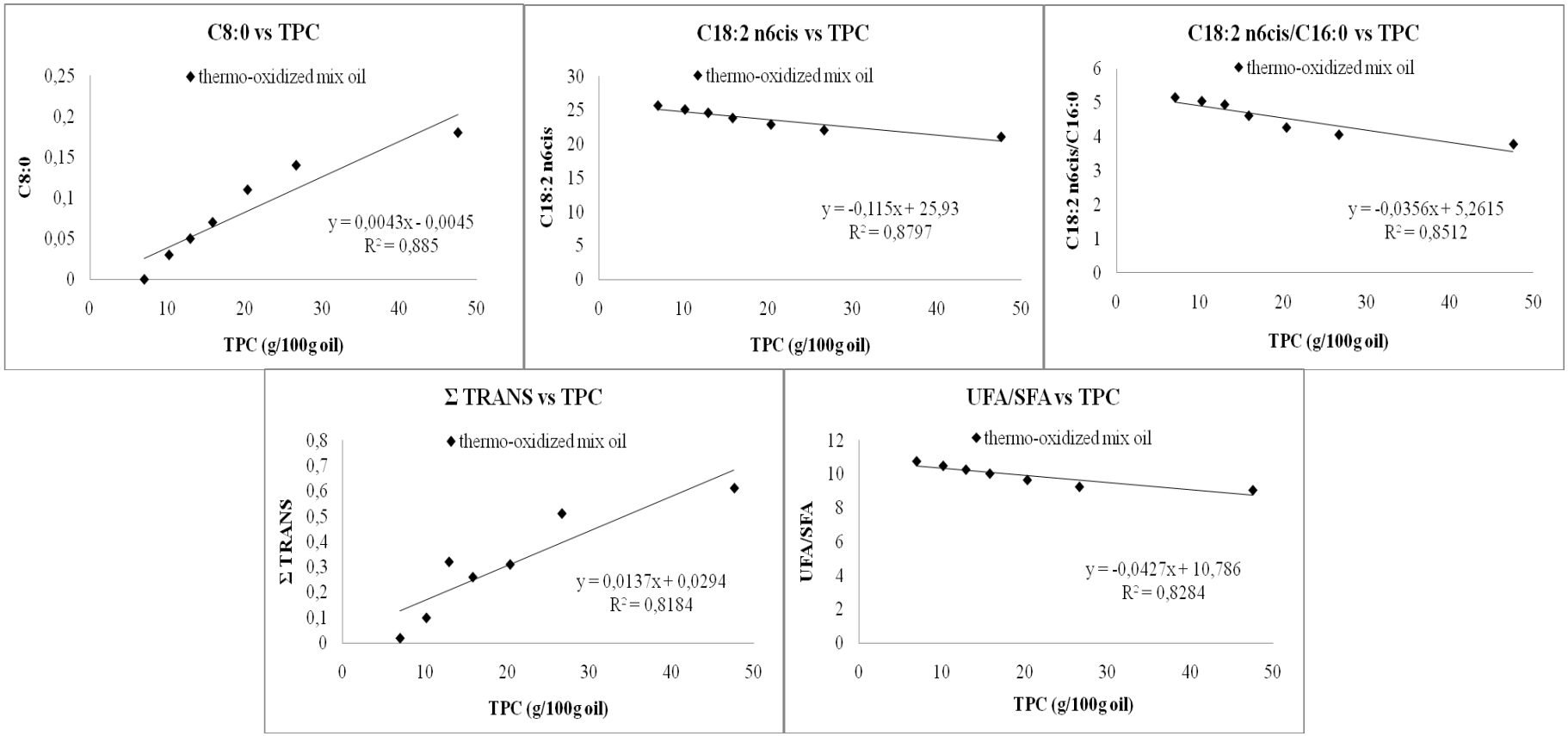

Fig. 3.13-Correlations between TPC and C8:0, C18:2 n6cis, C18:2 n6cis/c16:0, ΣTRANS and UFA/SFA in thermo-oxidized mix oil samples.

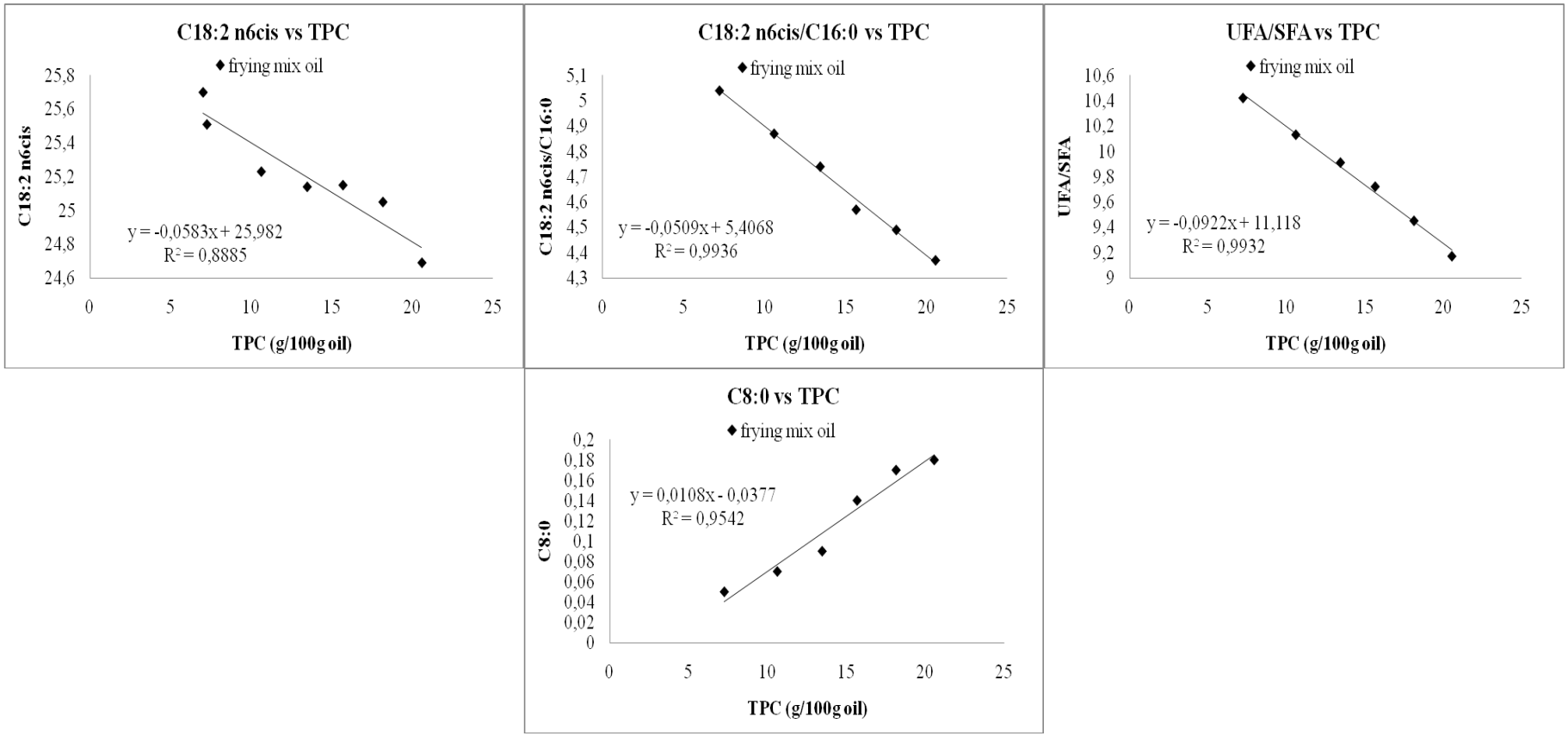

Fig. 3.14-Correlations between TPC and C18:2 n6cis, and between TPC and C8:0, C18:2 n6cis/c16:0 and UFA/SFA (without values at time 0) in frying mix oil samples.

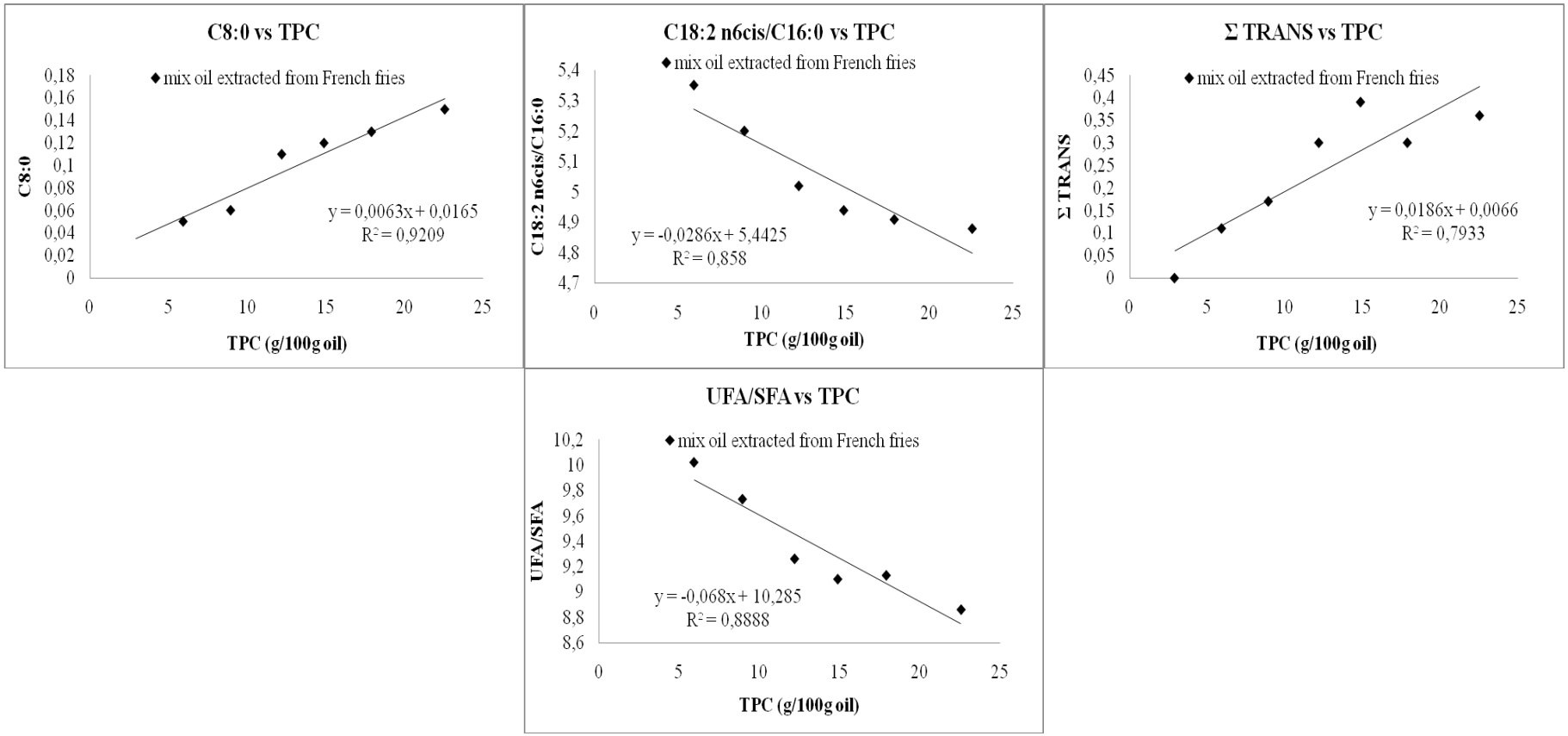

Fig. 3.15-Correlations between TPC and C8:0 and Σtrans and between TPC and C18:2 n6cis/c16:0 and UFA/SFA (without values at time 0) in mix oil extracted from French fries.

Tab. 3.25- VOCs concentration (ppb) of thermo-oxidized bi-fractionated palm oil at different treatment times.

THERMO-OXIDIZED BI-FRACTIONATED PALM OIL								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	-	-	-	-	114.42^{a}±8.51	112.89^{a}±7.60	144.21^{b}±10.73
	methyl cyclohexane	0.93±0.07	-	-	-	-	-	-
	propyl cyclohexane	-	0.62^{a}±0.05	0.53^{a}±0.04	1.46^{b}±0.11	1.48^{b}±0.11	1.36^{b}±0.09	2.17^{c}±0.17
	buthyl cyclopentane	-	2.90^{a}±0.22	2.89^{a}±0.20	4.07^{b}±0.30	3.03^{a}±0.21	3.57^{ab}±0.24	5.36^{c}±0.39
	propylcyclopentane	-	-	-	-	1.37±0.10	1.38±0.10	1.60±0.12
	decane	-	1.04±0.07	1.09±0.07	1.49±0.11	1.27±0.09	1.30±0.09	1.37±0.85
Σ		0.93	4.56	4.51	7.02	7.15	7.61	10.5
Alkenes	1-octene	-	-	-	-	-	4.12^{a}±0.27	6.88^{b}±0.51
	2-E-octene	-	0.76^{a}±0.05	0.48^{b}±0.03	-	-	-	-
Σ		-	0.76	0.48	-	-	4.12	6.88
Alcohols	1-pentanol	-	-	-	-	10.67±0.79	9.66±0.72	-
	1-hexanol	-	3.54^{a}±0.26	3.03^{a}±0.21	4.51^{b}±0.33	2.08^{c}±0.15	1.77^{c}±0.12	1.77^{c}±0.13
	1-heptanol	-	1.37^{a}±0.10	1.27^{a}±0.09	1.95^{bc}±0.14	1.99^{bc}±0.15	1.53^{ab}±0.10	2.28^{c}±0.17
	1-octen-3-ol	-	3.39^{a}±0.25	1.65^{b}±0.11	2.14^{b}±0.16	1.69^{b}±0.11	1.02^{c}±0.07	1.89^{b}±0.14
	1-octanol	-	1.20^{a}±0.09	0.13^{b}±0.01	1.18^{a}±0.09	1.20^{a}±0.10	0.68^{c}±0.05	1.39^{a}±0.11
Σ		-	9.50	6.08	9.78	17.63	14.66	7.33
Alkanals	hexanal	2.47^{a}±0.17	109.87^{bc}±8.18	95.04^{c}±6.40	111.81^{bc}±7.53	132.28^{b}±9.84	124.74^{bc}±8.40	179.33^{d}±13.35
	heptanal	-	11.62^{a}±0.86	11.02^{a}±0.74	13.83^{a}±1.03	14.11^{a}±1.05	13.53^{a}±0.92	23.86^{b}±1.77
	octanal	0.24^{a}±0.01	6.00^{bc}±0.45	5.43^{c}±0.37	8.51^{d}±0.64	8.04^{bd}±0.60	6.80^{bcd}±0.46	12.47^{e}±0.93
	nonanal	0.86^{a}±0.06	16.43^{bc}±1.22	13.06^{b}±0.88	17.99^{cd}±1.33	19.24^{cd}±1.43	12.91^{b}±0.87	21.75^{d}±1.62
	decanal	-	1.13^{ab}±0.08	0.71^{c}±0.05	0.96^{abc}±0.07	2.01^{d}±0.15	0.88^{ac}±0.06	1.21^{b}±0.09
	dodecanal	-	0.11^{a}±0.00	0.09^{a}±0.01	0.10^{a}±0.01	0.41^{b}±0.03	-	-
Σ		3.57	147.16	125.35	153.2	176.09	147.86	238.62
Alkenals	2-E-hexenal	-	2.95^{a}±0.22	2.51^{ab}±0.17	2.13^{b}±0.14	2.74^{ab}±0.21	2.62^{ab}±0.18	3.94^{c}±0.29
	2-Z-heptenal	-	16.42^{ab}±1.22	13.93^{a}±0.94	15.28^{a}±1.14	15.11^{a}±1.12	12.73^{a}±0.86	20.04^{b}±1.49
	2-E-octenal	-	4.77^{ab}±0.36	4.05^{ab}±0.27	4.81^{ab}±0.36	3.75^{b}±0.25	2.55^{c}±0.17	5.02^{a}±0.38

	2-E-nonenal	-	1.37^{ab}±0.10	1.43^{ab}±0.10	2.29^{cd}±0.17	1.81^{ac}±0.13	1.12^{b}±0.08	2.49^{d}±0.18
	2-E-decenal	-	8.53^{a}±0.63	4.83^{bc}±0.33	5.88^{b}±0.44	6.25^{b}±0.46	3.65^{c}±0.25	6.23^{b}±0.47
	2-undecenal	-	5.19±0.39	4.27±0.29	2.92±1.72	5.43±0.41	2.86±0.19	4.31±0.32
Σ		-	39.23	31.02	33.31	35.09	25.53	42.03
Alkadienals	2,4-E,E-heptadienal	-	1.40^{a}±0.10	0.79^{b}±0.06	1.12^{c}±0.08	0.56^{bd}±0.03	0.39^{d}±0.03	0.52^{d}±0.04
	2,4-E,E-nonadienal	-	0.20^{ab}±0.02	0.17^{b}±0.02	0.21^{a}±0.02	-	-	-
	2,4-E,E-decadienal	-	5.34^{a}±0.40	5.15^{a}±0.38	3.80^{b}±0.26	3.67^{bc}±0.28	1.55^{d}±0.11	2.62^{c}±0.20
Σ		-	6.94	6.11	5.13	4.23	1.94	3.14
Ketones	2-heptanone	-	4.25^{a}±0.32	2.93^{b}±0.21	3.56^{ab}±0.26	3.17^{b}±0.24	2.82^{b}±0.19	5.67^{c}±0.43
Acids	esanoic acid	-	2.30±0.17	-	-	-	-	-
	octanoic acid	-	10.82±0.81	-	-	-	-	-
	butanedioic acid methyl bis (1-methylpropyl) ester	-	0.33^{a}±0.02	0.33^{a}±0.02	0.33^{a}±0.02	1.59^{b}±0.12	0.25^{a}±0.02	0.19^{a}±0.01
Σ		-	13.45	0.33	0.33	1.59	0.25	0.19
Arom. eterocyclic Hydroc.	2-pentyl furan	-	9.40^{ab}±0.70	9.35^{ab}±0.63	13.51^{c}±1.00	11.26^{ac}±0.75	7.75^{b}±0.52	17.72^{d}±1.31
	2n-heptyl furan	-	0.47^{a}±0.04	0.44^{a}±0.03	0.77^{b}±0.05	0.70^{b}±0.05	0.38^{a}±0.03	0.84^{b}±0.06
	2n-octyl furan	-	-	-	1.68^{a}±0.13	2.15^{b}±0.16	1.18^{c}±0.08	1.49^{ac}±0.11
Σ		-	9.87	9.79	15.96	14.11	9.31	20.05
Ethers	esil pentil etere	-	-	0.34^{a}±0.02	0.45^{b}±0.04	0.33^{a}±0.02	0.22^{c}±0.01	0.39^{ab}±0.03

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.
- under detection limit (<0.01%)

Tab. 3.26- VOCs concentration (ppb) of frying bi-fractionated palm oil at different treatment times.

FRYING BI-FRACTIONATED PALM OIL								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	-	$23.43^{a}\pm1.58$	$37.31^{b}\pm2.51$	$71.97^{c}\pm5.35$	$12.06^{d}\pm0.81$	$38.64^{b}\pm2.88$	$42.16^{b}\pm2.84$
	methyl cyclohexane	0.93±0.07	-	-	-	-	-	-
	propyl cyclohexane	-	$0.39^{a}\pm0.03$	$0.31^{a}\pm0.02$	$0.51^{b}\pm0.03$	$0.21^{c}\pm0.01$	$0.41^{a}\pm0.03$	$0.37^{a}\pm0.03$
	buthyl cyclopentane	-	$1.10^{a}\pm0.08$	$1.23^{a}\pm0.08$	$2.05^{b}\pm0.16$	$0.43^{c}\pm0.03$	$0.97^{a}\pm0.07$	$1.06^{a}\pm0.07$
Σ		0.93	24.92	38.85	74.53	12.7	40.02	43.59
Alkenes	1-octene	-	$1.60^{a}\pm0.12$	$1.61^{a}\pm0.10$	$3.05^{b}\pm0.23$	$1.23^{a}\pm0.09$	$2.89^{b}\pm0.21$	$2.53^{b}\pm0.17$
Alcohols	1-pentanol	-	$3.16^{a}\pm0.21$	$4.65^{b}\pm0.31$	$7.51^{c}\pm0.56$	$1.81^{d}\pm0.12$	$3.04^{a}\pm0.23$	$3.57^{ab}\pm0.24$
	4-methyl-1-pentanol	-	$1.08^{a}\pm0.08$	$0.79^{b}\pm0.06$	$1.45^{c}\pm0.11$	$0.49^{d}\pm0.03$	$1.07^{a}\pm0.08$	$0.67^{bd}\pm0.04$
	heptanol	-	$0.42^{a}\pm0.03$	$0.64^{b}\pm0.04$	$0.79^{c}\pm0.06$	$0.32^{a}\pm0.02$	$0.60^{b}\pm0.04$	$0.60^{b}\pm0.5$
	1-octen-3-ol	-	$0.72^{ab}\pm0.05$	$0.92^{b}\pm0.07$	$1.23^{c}\pm0.09$	$0.54^{a}\pm0.04$	$0.78^{b}\pm0.05$	$0.76^{ab}\pm0.05$
	1-octanol	-	$0.25^{a}\pm0.01$	$0.39^{b}\pm0.03$	$0.56^{c}\pm0.04$	$0.27^{a}\pm0.02$	$0.38^{b}\pm0.03$	$0.39^{b}\pm0.03$
Σ		-	5.63	7.39	11.54	3.43	5.87	5.99
Alkanals	hexanal	$2.47^{a}\pm0.17$	$48.52^{b}\pm3.27$	$61.17^{bc}\pm4.13$	$95.75^{d}\pm7.13$	$28.70^{e}\pm1.93$	$62.14^{bc}\pm4.63$	$65.49^{c}\pm4.41$
	heptanal	-	$3.74^{a}\pm0.25$	$5.80^{b}\pm0.39$	$8.19^{c}\pm0.61$	$2.69^{a}\pm0.18$	$5.59^{b}\pm0.42$	$5.94^{b}\pm0.41$
	octanal	$0.24^{a}\pm0.01$	$2.18^{b}\pm0.15$	$3.64^{c}\pm0.25$	$5.16^{d}\pm0.25$	$2.06^{b}\pm0.14$	$3.66^{c}\pm0.27$	$4.15^{c}\pm0.28$
	nonanal	$0.86^{a}\pm0.06$	$10.20^{b}\pm0.69$	$11.42^{b}\pm0.77$	$14.12^{c}\pm1.05$	$5.42^{d}\pm0.37$	$9.27^{b}\pm0.70$	$9.53^{b}\pm0.64$
	decanal	-	$0.35^{ab}\pm0.02$	$0.38^{ac}\pm0.03$	$0.56^{d}\pm0.04$	$0.24^{b}\pm0.01$	$0.48^{cd}\pm0.04$	$0.46^{cd}\pm0.03$
Σ		3.57	64.99	82.41	123.78	39.11	81.14	85.57
Alkenals	2-E-hexenal	-	$0.74^{ab}\pm0.05$	$1.58^{c}\pm0.11$	$2.00^{d}\pm0.15$	$0.59^{a}\pm0.04$	$1.03^{be}\pm0.08$	$1.24^{e}\pm0.09$
	2-Z-heptenal	-	$6.18^{ab}\pm0.42$	$9.29^{c}\pm0.63$	$12.10^{d}\pm0.90$	$4.45^{a}\pm0.30$	$7.39^{bc}\pm0.55$	$7.61^{bc}\pm0.52$
	2-E-octenal	-	$2.07^{a}\pm0.14$	$2.37^{ab}\pm0.16$	$2.80^{b}\pm0.21$	$1.35^{c}\pm0.09$	$1.99^{a}\pm0.15$	$2.13^{a}\pm0.14$
	2-E-nonenal	-	$0.53^{a}\pm0.03$	$0.62^{a}\pm0.04$	$1.03^{b}\pm0.08$	$0.50^{a}\pm0.03$	$0.92^{b}\pm0.07$	$1.04^{b}\pm0.07$
	2-E-decenal	-	$2.44^{ab}\pm0.16$	$3.18^{ac}\pm0.21$	$4.71^{d}\pm0.35$	$2.08^{b}\pm0.14$	$3.62^{c}\pm0.27$	$3.27^{ac}\pm0.22$
	2 -undecenal	-	$1.72^{a}\pm0.12$	$2.58^{b}\pm0.17$	$3.72^{c}\pm0.27$	$1.71^{a}\pm0.11$	$3.06^{bc}\pm0.23$	$2.71^{b}\pm0.19$
Σ		-	13.68	19.62	26.36	10.68	18.01	18.00

Alkadienals	2,4-E,E-heptadienal	-	0.58^{a}±0.04	0.30^{b}±0.02	-	-	-	-
	2,4-E,E-decadienal	-	5.13^{a}±0.38	5.01^{a}±0.34	4.84^{a}±0.36	2.70^{b}±0.19	4.22^{ac}±0.31	3.27^{bc}±0.22
Σ		-	5.71	5.61	4.84	2.70	4.22	3.27
Ketones	2-ehptanone	-	0.97^{a}±0.06	1.45^{b}±0.10	2.12^{c}±0.16	0.66^{a}±0.04	1.40^{b}±0.10	1.51^{b}±0.10
Acids	butanedioic acid methyl bis (1-methylpropyl) ester	-	0.32^{a}±0.02	0.27^{a}±0.02	0.62^{b}±0.04	0.35^{a}±0.02	0.34^{a}±0.02	0.46^{c}±0.03
Arom. Eterocyclic Hydr.	2-pentyl furan	-	3.40^{a}±0.23	4.50^{bc}±0.30	4.77^{b}±0.35	1.67^{d}±0.11	3.27^{a}±0.24	3.69^{ac}±0.24

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.27- VOCs concentration (ppb) of bi-fractionated palm oil extracted from French fries at different treatment times.

BI-FRACTIONATED PALM OIL EXTRACTED FROM FRENCH FRIES								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	dodecane	0.81^{a}±0.06	2.38^{b}±0.17	1.49^{c}±0.10	1.66^{c}±0.12	2.86^{b}±0.21	2.28^{b}±0.16	2.37^{c}±0.16
	2,6-dimethyl undecane	0.18±0.08	-	-	-	0.21±0.01	-	-
	eicosane	-	0.14^{a}±0.01	0.12^{a}±0.01	0.14^{a}±0.01	0.35^{b}±0.03	0.21^{c}±0.02	0.14^{a}±0.01
Σ		0.99	2.52	1.61	1.18	3.42	2.49	2.51
Alkanals	hexanal	4.44±0.33	3.95±0.27	-	-	-	-	-
	nonanal	1.97^{a}±0.08	2.44^{ab}±0.16	3.03^{b}±0.21	2.92^{ab}±0.22	2.87^{ab}±0.19	3.37^{b}±0.23	6.37^{a}±0.47
	decanal	0.15^{a}±0.01	0.15^{a}±0.01	0.17^{a}±0.01	0.29^{b}±0.02	0.22^{ab}±0.02	0.30^{b}±0.02	0.81^{c}±0.05
	dodecanal	-	-	0.06^{a}±0.01	0.08^{ab}±0.01	0.14^{c}±0.01	0.11^{bc}±0.00	0.26^{d}±0.02
Σ		6.56	6.54	3.26	3.29	3.23	3.78	7.44
Alkenals	2-E-nonenal	0.33^{a}±0.02	0.49^{ab}±0.03	0.64^{bc}±0.05	0.43^{a}±0.03	0.62^{bc}±0.04	0.62^{bc}±0.04	0.78^{c}±0.06
	2-E-decenal	0.88^{a}±0.06	1.57^{b}±0.11	0.08^{c}±0.01	1.99^{b}±0.15	2.05^{b}±0.15	2.13^{b}±0.14	4.68^{d}±0.35
	2-undecenal	0.74^{a}±0.05	1.35^{ab}±0.10	1.80^{bc}±0.12	2.40^{c}±0.16	2.33^{c}±0.17	2.18^{c}±0.15	4.56^{d}±0.34
Σ		1.95	3.41	2.52	4.82	5.00	4.93	10.02
Alkadienals	2,4-E,E-nonadienal	-	-	-	-	-	-	0.28±0.02
	2,4-E,E-decadienal	1.42^{a}±0.13	2.47^{b}±0.19	2.30^{b}±0.17	1.92^{ab}±0.14	1.65^{a}±0.12	1.64^{a}±0.12	3.23^{c}±0.24
Σ		1.42	2.47	2.30	1.92	1.65	1.64	3.51
Ketones	cicloesanone, 2-metil 5-(1metiletenil) trans	-	0.34^{a}b±0.03	0.30^{b}±0.02	0.29^{b}±0.02	0.74^{c}±0.06	0.43^{a}±0.03	0.10^{d}±0.00
Acids	butanoic, 2-methyl acid	-	4.71^{a}±0.36	3.55^{ab}±0.24	12.82^{c}±0.96	2.56^{b}±0.17	3.15^{ab}±0.23	-
	hexanoic acid	0.74^{ab}±0.09	0.92^{ab}±0.07	0.79^{ab}±0.06	0.54^{b}±0.03	1.75^{c}±0.13	1.06^{a}±0.07	3.18^{d}±0.24
	octanoic acid	-	-	-	-	-	-	0.92±0.06
	butanedioic acid methyl bis (1-methylpropyl) ester	0.35^{a}±0.03	0.34^{a}±0.03	0.37^{a}±0.03	0.72^{b}±0.06	0.79^{b}±0.06	0.64^{b}±0.05	0.41^{a}±0.03
Σ		1.09	5.97	4.71	14.08	5.10	4.85	4.51
Arom. Eterociclyc Hydr.	2,5-dimethyl pyrazine	-	0.47±0.04	-	-	-	-	-
	2-pentyl furan	0.58±0.06	0.58±0.05	0.55±0.04	0.55±0.04	-	-	-
Σ		0.58	1.05	0.55	0.55	-	-	-

Aromatic Hydr.	*o*-xylene	0.90^{a}±0.04	1.03^{a}±0.08	0.46^{b}±0.03	0.51^{b}±0.03	1.00^{a}±0.07	1.59^{c}±0.12	0.46^{b}±0.03
	styrene	2.45^{ab}±0.16	2.62^{ab}±0.19	2.68^{ab}±0.18	3.31^{a}±0.22	5.39^{c}±0.41	6.58^{d}±0.49	1.69^{b}±0.11
Σ		3.35	3.65	3.14	3.82	6.39	8.17	5.01
Monoterpenes arom.	D limonene	3.50^{a}±0.42	4.19^{ab}±0.31	3.98^{ab}±0.27	4.94^{ab}±0.37	5.19^{bc}±0.34	6.41^{b}±0.48	5.01^{bc}±0.34

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.28- VOCs concentration (ppb) of thermo-oxidized olive oil at different treatment times.

THERMO-OXIDIZED OLIVE OIL								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	23.15^{a}±0.68	114.62^{b}±24.57	156.85^{bc}±9.09	150.72^{bc}±10.39	139.31^{bc}±6.41	169.80^{c}±12.13	147.33^{c}±4.31
	octane	-	73.82±17.62	73.03±2.99	57.40±4.50	55.33±0.07	47.40±3.83	59.81±0.14
	propyl cyclohexane	-	1.32^{ac}±0.17	1.84^{b}±0.09	1.18^{ac}±0.11	1.47^{ab}±0.06	1.02^{c}±0.09	1.04^{c}±0.03
	buthyl cyclopentane	-	4.23^{a}±0.64	5.21^{a}±0.36	4.19^{a}±0.03	4.21^{a}±0.05	2.71^{b}±0.06	3.66^{c}±0.47
Σ		23.15	193.99	236.93	213.49	200.32	220.93	211.84
Alkenes	1-methyl-4-(1methylethyl) cyclohexene	-	1.32^{a}±0.23	1.41^{a}±0.05	0.80^{b}±0.00	0.77^{b}±0.00	0.42^{b}±0.01	0.45^{b}±0.01
	2-methyl-3-ethyl 1,3-hexadiene	-	1.01^{a}±0.28	0.46^{bc}±0.06	0.31^{c}±0.03	0.78^{ac}±0.01	-	-
Σ		-	2.33	1.87	1.11	1.55	0.42	0.45
Alcohol	1-pentanol	-	10.56^{ac}±1.58	16.70^{b}±1.27	13.86^{ab}±0.71	7.61^{cd}±1.01	5.85^{d}±0.23	7.59^{c}±0.31
	1-hexanol	-	1.41^{ac}±0.20	1.98^{b}±0.06	1.51^{ac}±0.09	1.63^{ab}±0.08	1.17^{c}±0.09	1.58^{ac}±0.05
	heptanol	-	2.40^{a}±0.13	3.50^{b}±0.25	3.06^{b}±0.16	3.31^{b}±0.04	2.02^{a}±0.03	2.62^{a}±0.07
	1-octen-3-ol	-	4.69^{ab}±0.60	5.37^{a}±0.28	4.10^{bc}±0.26	3.44^{c}±0.03	2.97^{c}±0.24	2.43^{c}±0.19
	1-octanol	0.07^{a}±0.01	2.23^{bc}±0.44	2.91^{c}±0.19	2.47^{bc}±0.02	2.60^{bc}±0.16	1.98^{b}±0.15	2.24^{bc}±0.18
Σ		0.07	21.29	30.46	25.00	18.59	13.99	16.46
Alkanals	hexanal	4.88^{a}±1.02	60.44^{b}±12.28	66.68^{b}±0.49	63.79^{b}±4.88	59.36^{b}±3.90	45.30^{b}±1.21	53.07^{b}±0.95
	heptanal	0.45^{a}±0.16	11.51^{b}±1.92	15.66^{c}±0.92	12.85^{bc}±0.75	14.39^{bc}±1.15	10.99^{b}±0.10	11.64^{b}±0.63
	octtanal	0.65^{a}±0.14	6.53^{b}±0.85	9.27^{c}±0.29	8.28^{c}±0.29	8.78^{c}±0.01	6.65^{b}±0.08	8.41^{c}±0.11
	nonanal	2.34^{a}±0.61	23.63^{b}±5.71	27.28^{b}±1.76	23.21^{b}±2.74	24.26^{b}±0.92	17.85^{bc}±1.20	19.39^{bc}±1.32
	decanal	0.09^{a}±0.00	0.74^{b}±0.14	0.91^{b}±0.24	0.82^{b}±0.14	0.82^{b}±0.03	0.66^{b}±0.07	0.66^{b}±0.05
	4-oxononanal	-	-	-	-	1.44^{a}±0.20	0.54^{b}±0.77	0.81^{b}±0.01
	dodecanal	-	0.19^{a}±0.04	0.34^{b}±0.07	-	-	-	-
Σ		8.41	103.04	120.14	108.95	109.05	81.99	93.98
Alkenals	2-E-hexenal	-	4.14^{ab}±0.52	4.69^{a}±0.33	3.49^{b}±0.22	3.23^{b}±0.09	2.02^{c}±0.02	2.40^{c}±0.12
	2-Z-heptenal	0.38^{a}±0.00	21.81^{bc}±3.64	24.88^{b}±1.36	17.87^{c}±0.21	16.90^{cd}±0.44	10.80^{d}±0.20	12.06^{d}±0.34
	2-E-octenal	-	6.28^{ab}±1.47	6.71^{a}±0.67	5.33^{ab}±0.41	5.37^{ab}±0.15	3.61^{bc}±0.05	4.11^{bc}±0.07
	2-E-nonenal	-	2.63±0.66	3.89±0.21	3.21±0.03	3.78±0.26	2.74±0.32	3.17±0.45

	2-E-decenal	0.50^{a}±0.05	10.79^{b}±1.88	15.78^{b}±1.53	12.90^{b}±0.41	14.24^{b}±1.52	11.14^{b}±2.50	11.38^{b}±1.21
	2-undecenal	-	7.50^{a}±1.11	11.11^{a}±2.08	10.38^{a}±1.83	11.48^{a}±1.46	9.99^{a}±2.84	10.20^{a}±1.89
Σ		0.88	53.15	67.06	53.18	55.00	40.30	43.32
Alkadienals	2,4-E,E-heptadienal	-	2.81^{a}±0.36	3.05^{a}±0.11	1.73^{b}±0.01	1.66^{b}±0.06	0.91^{c}±0.03	0.86^{c}±0.09
	2,4-E,E-nonadienal	-	0.70^{b}±0.22	0.63^{b}±0.09	0.49^{b}±0.12	0.41^{ab}±0.02	0.30^{ab}±0.05	0.28^{a}±0.03
	2,4-E,E-dodecadienal	-	4.21^{a}±1.16	2.88^{ab}±0.23	2.78^{ab}±0.15	2.03^{b}±0.19	2.00^{b}±0.13	-
	2,4-E,E-decadienal	-	13.36^{a}±3.41	9.36^{ab}±0.61	6.56^{b}±0.91	6.08^{b}±0.88	4.53^{b}±1.21	3.81^{bc}±0.90
Σ		-	21.08	15.92	11.56	10.18	7.74	4.95
Ketones	2-heptanone	0.21^{a}±0.03	2.24^{b}±0.36	4.08^{c}±0.34	3.79^{c}±0.19	3.41^{c}±0.32	2.24^{b}±0.07	3.27^{c}±0.08
	3-octanone	-	-	-	0.53^{a}±0.01	0.53^{a}±0.08	0.28^{b}±0.02	0.39^{c}±0.14
	2-propylcyclopentanone	-	1.00^{a}±0.25	2.10^{b}±0.98	0.*65*^{a}±0.35	0.71^{a}±0.06	0.40^{a}±0.00	-
Σ		0.21	3.24	6.81	4.97	4.65	2.92	3.66
Acids	hexanoic acid	0.35^{a}±0.02	4.89^{b}±1.37	1.69^{a}±0.37	2.28^{a}±0.13	1.91^{a}±0.04	0.87^{a}±0.09	-
	octanoic acid	-	1.11^{a}±0.30	3.53^{b}±1.74	1.60^{a}±0.11	1.04^{a}±0.15	0.69^{a}±0.05	-
	butanedioic acid methyl bis (1-methylpropyl) ester	0.24^{a}±0.07	0.49^{b}±0.03	0.65^{b}±0.00	0.50^{b}±0.04	0.57^{b}±0.01	0.93^{bc}±0.10	1.16^{bc}±0.09
Σ		0.59	6.49	5.87	4.38	3.52	2.44	1.16
Arom. eterocyclic Hydr..	2-pentyl furan	0.43^{a}±0.00	5.87^{b}±0.95	8.91^{c}±0.00	7.65^{c}±0.0	8.12^{c}±0.40	4.93^{b}±0.08	6.50^{bc}±0.87
	hexyl furan	-	-	0.63^{a}±0.03	0.64^{a}±0.03	0.89^{b}±0.09	0.57^{a}±0.04	0.78^{b}±0.34
	2n-heptyl furan	-	-	1.07^{a}±0.03	0.86^{bc}±0.01	1.05^{a}±0.05	0.88^{bc}±0.09	1.00^{a}±0.06
Σ		0.43	5.87	10.61	9.15	10.06	6.38	8.28
Monoterpenes arom.	D limonene	-	0.24^{a}±0.00	0.44^{b}±0.01	0.92^{c}±0.06	-	0.26^{a}±0.03	0.16^{a}±0.02

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.29- VOCs concentration (ppb) of frying olive oil different treatment times.

FRYING OLIVE OIL								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	23.15^{a}±0.68	76.04^{ab}±5.00	34.69^{a}±4.47	61.98^{a}±7.12	35.47^{a}±1.37	146.62^{b}±54.29	26.01^{a}±6.40
	propyl cyclohexane	-	0.34^{a}±0.05	0.19^{bc}±0.05	0.23^{ab}±0.00	0.25^{ab}±0.02	0.09^{c}±0.01	-
	buthyl cyclopentane	-	0.94^{a}±0.02	0.65^{b}±0.13	0.93^{a}±0.10	0.65^{b}±0.04	0.40^{bc}±0.05	0.15^{c}±0.03
Σ		23.15	77.32	35.53	63.14	36.37	147.11	26.16
Akenes	1-methyl-4 (1methylethyl)-cyclohexene	-	0.24^{a}±0.00	0.14^{b}±0.02	0.13^{bc}±0.01	0.10^{c}±0.01	0.06^{d}±0.01	-
Alcohol	heptanol	-	0.46^{a}±0.01	0.38^{ab}±0.08	0.48^{a}±0.05	0.37^{ab}±0.04	0.29^{b}±0.03	0.30^{b}±0.01
	1-octen-3-ol	-	0.45±0.64	0.57±0.01	0.89±0.21	0.60±0.01	0.49±0.00	0.29±0.41
	1-octanol	0.07^{a}±0.01	0.41^{bc}±0.03	0.31^{c}±0.07	0.35^{c}±0.07	0.29^{c}±0.05	0.24^{ac}±0.02	0.52^{b}±0.01
Σ		0.07	1.32	1.26	1.72	1.26	1.02	1.11
Alkanals	hexanal	4.88^{a}±1.02	48.69^{bc}±2.63	40.48^{bcd}±9.08	57.72^{b}±6.66	43.71^{bcd}±3.53	29.04^{d}±2.84	38.67^{cd}±1.14
	heptanal	0.45^{a}±0.16	2.88^{bc}±0.15	2.51^{c}±0.43	3.63^{b}±0.29	2.88^{bc}±0.08	2.13^{c}±0.18	2.81^{bc}±0.00
	octanal	0.65±0.14	2.26±0.08	1.82±0.39	2.55±0.46	2.26±0.27	1.73±0.09	2.11±0.16
	nonanal	2.34^{a}±0.61	8.30^{b}±0.09	6.20^{b}±1.60	7.18^{b}±0.88	6.81^{b}±0.88	5.01^{ab}±0.26	6.65^{b}±1.31
	decanal	0.09±0.00	0.18±0.07	0.26±0.07	0.21±0.07	0.22±0.01	0.21±0.02	0.22±0.11
Σ		8.41	62.31	51.27	71.29	55.88	38.12	50.46
Alkenals	2-E-hexenal	-	1.45^{a}±0.04	1.03^{bc}±0.21	1.29^{ab}±0.13	1.02^{bc}±0.09	0.66^{c}±0.04	0.68^{c}±0.08
	2-E-heptenal	-	6.10^{a}±0.02	4.67^{abc}±0.83	5.50^{ab}±0.23	4.52^{bc}±0.37	3.22^{c}±0.30	3.57^{c}±0.12
	2-Z- heptenal	0.38±0.00	-	-	-	-	-	-
	2-E-octenal	-	1.12±0.00	0.91±0.20	1.08±0.18	1.06±0.11	0.81±0.05	1.03±0.01
	2-E- nonenal	-	0.62^{a}±0.00	0.46^{ab}±0.09	0.50^{ab}±0.04	0.47^{ab}±0.04	0.40^{b}±0.06	0.51^{ab}±0.00
	2-E-decenal	0.50^{a}±0.05	3.26^{b}±0.05	2.50^{b}±0.22	2.65^{b}±0.19	2.19^{b}±0.17	2.06^{b}±0.52	2.10^{b}±0.54
	2- undecenal	-	2.66±0.16	2.12±0.05	2.36±0.14	2.01±0.09	2.08±0.41	1.81±0.57
Σ		0.88	15.21	11.69	13.38	11.27	9.23	9.70
Alkadienals	2,4-E,E-heptadienal	-	1.22^{a}±0.08	0.55^{b}±0.03	0.31^{c}±0.03	0.32^{c}±0.00	0.19^{c}±0.03	0.23^{c}±0.07

	2,4-E,E-decadienal	-	3.07^{a}±0.15	2.37^{ab}±0.30	2.52^{ab}±0.01	2.27^{abc}±0.17	1.80^{bc}±0.22	1.38^{c}±0.43
Σ		-	4.29	3.82	2.83	2.59	1.99	1.61
Ketones	2 -heptanone	0.21^{a}±0.03	0.45^{ab}±0.04	0.49^{b}±0.10	0.66^{b}±0.04	0.55^{b}±0.03	0.47^{b}±0.04	0.55^{b}±0.10
Acids	hexanoic acid	0.35±0.02	1.01±1.09	0.63±0.32	0.71±0.25	0.84±0.43	0.39±0.00	1.07±1.09
	butanedioic acid methyl bis (1-methylpropyl) ester	0.24^{a}±0.07	0.31^{ab}±0.01	0.73^{b}±0.04	0.13^{a}±0.18	0.26^{ab}±0.01	0.21^{a}±0.01	0.18^{a}±0.25
Σ		0.59	1.32	1.36	0.84	1.10	0.60	1.25
Arom. eterocyclic hydr.	2-pentyl furan	0.43^{a}±0.00	0.69^{ab}±0.03	0.69^{ab}±0.14	1.04^{bc}±0.12	1.03^{bc}±0.12	0.81^{ab}±0.03	1.26^{c}±0.12

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.30- VOCs concentration (ppb) of olive oil extracted from French fries at different treatment times.

OLIVE OIL EXTRACTED FROM FRENCH FRIES								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	nonane	$0.38^{a} \pm 0.05$	$3.24^{b} \pm 0.21$	$0.42^{a} \pm 0.02$	$0.46^{a} \pm 0.04$	$0.54^{a} \pm 0.00$	$0.77^{a} \pm 0.48$	$1.28^{a} \pm 0.54$
	decane	-	$1.81^{a} \pm 0.06$	$0.16^{b} \pm 0.00$	$0.18^{b} \pm 0.05$	-	-	-
	dodecane	$0.81^{a} \pm 0.06$	$5.83^{bc} \pm 0.42$	$4.85^{abc} \pm 0.19$	$5.14^{abc} \pm 0.16$	$1.87^{ac} \pm 0.22$	$7.17^{b} \pm 3.12$	$2.33^{ac} \pm 0.36$
	hexylcyclohexane	-	$1.86^{ab} \pm 0.03$	$1.47^{abc} \pm 0.02$	$1.63^{ab} \pm 0.06$	$0.52^{b} \pm 0.02$	$2.34^{a} \pm 1.02$	$0.77^{ab} \pm 0.20$
	cis decalyn 2syn methyl	-	$0.93^{a} \pm 0.07$	$1.46^{b} \pm 0.13$	$0.80^{ac} \pm 0.22$	$0.22^{d} \pm 0.01$	$0.95^{a} \pm 0.20$	$0.32^{cd} \pm 0.04$
	cis decalyn 1syn methyl	-	$0.48^{a} \pm 0.00$	$0.34^{ab} \pm 0.02$	$0.32^{ab} \pm 0.04$	$0.12^{b} \pm 0.00$	$0.51^{a} \pm 0.19$	$0.15^{b} \pm 0.01$
	2,6-dimethyl undecane	$0.18^{a} \pm 0.08$	$2.31^{bc} \pm 0.21$	$1.92^{abc} \pm 0.01$	$2.34^{bc} \pm 0.33$	$0.73^{ac} \pm 0.01$	$2.99^{b} \pm 1.30$	$1.03^{abc} \pm 0.13$
	trans, trans-1,6-dimethylspiro(4.5)decane	-	$1.48^{a} \pm 0.10$	$0.77^{b} \pm 0.07$	$1.23^{a} \pm 0.11$	-	-	-
	cis, cis 3ethylbicyclo(4.4.0)decane	-	$1.19^{ab} \pm 0.09$	$1.11^{b} \pm 0.05$	$1.06^{b} \pm 0.03$	$0.26^{c} \pm 0.02$	$1.46^{a} \pm 0.16$	$0.50^{c} \pm 0.06$
	cyclododecane	-	-	0.60 ± 0.03	0.44 ± 0.48	0.31 ± 0.02	0.97 ± 0.37	2.44 ± 1.80
	10-methyl nonadecane	-	-	$1.40^{ab} \pm 0.11$	$2.09^{ab} \pm 0.18$	$0.63^{b} \pm 0.13$	$3.15^{a} \pm 1.48$	-
	1,1-dimethyl cyclohexane	-	0.81 ± 0.03	0.70 ± 0.03	0.75 ± 0.19	0.25 ± 0.01	1.13 ± 0.59	0.38 ± 0.10
	4-methyldodecane	-	1.50 ± 0.07	1.41 ± 0.01	1.03 ± 0.18	0.38 ± 0.08	2.85 ± 2.55	-
	10-methyl nonadecane	-	-	$1.40^{ab} \pm 0.11$	$2.09^{ab} \pm 0.18$	$0.63^{b} \pm 0.13$	$3.15^{a} \pm 1.48$	-
	tridecane	-	$6.32^{ab} \pm 0.25$	$5.26^{ab} \pm 0.20$	$6.11^{ab} \pm 0.57$	$2.28^{b} \pm 0.19$	$9.25^{a} \pm 4.03$	$3.17^{ab} \pm 0.09$
	1,1-dimethyl cyclohexane	-	0.81 ± 0.03	0.70 ± 0.03	0.75 ± 0.19	0.25 ± 0.01	1.13 ± 0.59	0.38 ± 0.10
	1,1'-bicyclohexyl	-	0.74 ± 0.01	0.69 ± 0.01	0.65 ± 0.18	0.24 ± 0.04	1.10 ± 0.57	0.36 ± 0.08
	heptylcyclohexane	-	$1.76^{ab} \pm 0.04$	$1.15^{ab} \pm 0.07$	$1.10^{ab} \pm 0.06$	$0.65^{b} \pm 0.25$	$2.10^{a} \pm 0.23$	$2.10^{a} \pm 0.89$
	5-methyltridecane	-	0.59 ± 0.06	0.57 ± 0.00	0.58 ± 0.07	0.26 ± 0.01	0.86 ± 0.31	0.73 ± 0.42
	4-methyltridecane	-	$0.63^{ab} \pm 0.08$	$0.60^{ab} \pm 0.01$	$0.75^{ab} \pm 0.06$	$0.38^{b} \pm 0.21$	$1.21^{a} \pm 0.38$	$0.59^{ab} \pm 0.06$
	2-methyl tridecane	-	-	$0.72^{a} \pm 0.13$	$0.72^{a} \pm 0.15$	$0.13^{b} \pm 0.18$	-	-
	tetradecane	-	$3.48^{ab} \pm 0.41$	$2.90^{ab} \pm 0.28$	$3.17^{ab} \pm 0.29$	$1.47^{b} \pm 0.05$	$5.17^{a} \pm 2.36$	$2.22^{ab} \pm 0.27$
	pentadecane	-	2.52 ± 0.11	1.62 ± 0.07	1.97 ± 0.26	0.95 ± 0.17	4.06 ± 2.16	1.73 ± 0.09
	hexadecane	-	0.92 ± 0.04	0.40 ± 0.11	0.37 ± 0.20	0.34 ± 0.09	0.40 ± 0.57	-
	9-methyl nonadecane	-	$1.56^{ab} \pm 0.09$	$1.37^{ab} \pm 0.02$	$1.54^{ab} \pm 0.11$	$0.61^{b} \pm 0.05$	$2.76^{a} \pm 1.21$	-

	2,6,10-trimethyl dodecane	-	-	0.49^{ab} ± 0.03	0.70^{ab} ± 0.01	0.24^{b} ± 0.06	1.29^{a} ± 0.59	0.78^{ab} ± 0.09
Σ		1.37	36.96	32.38	35.13	13.38	52.49	20.88
Alkenes	1-hexene	-	-	0.14 ± 0.00	0.11 ± 0.02	-	-	-
	1-decene	-	3.56^{a} ± 0.32	2.29^{b} ± 0.00	-	-	-	-
	2,4,4-trimethyl-1-pentene	-	-	-	-	0.35^{a} ± 0.05	1.66^{b} ± 0.74	-
Σ		-	3.56	2.43	0.11	0.35	1.66	-
Alcohols	1-heptadecanol	-	2.09^{a} ± 0.30	1.52^{b} ± 0.07	-	-	-	-
	2-hexyl-1-decanol	-	-	0.74^{ab} ± 0.04	0.82^{ab} ± 0.04	0.43^{b} ± 0.11	1.20^{a} ± 0.42	0.61^{ab} ± 0.06
Σ		-	2.09	2.26	0.82	0.43	1.20	0.61
Alkanals	hexanal	4.44^{a}±0.33	195.20^{b} ± 1.41	7.10^{ac} ± 0.51	8.24^{ac} ± 3.46	19.40^{d} ± 1.19	11.63^{d} ± 1.74	71.88^{e} ± 13.89
	octanal	0.19 ± 0.01	0.24 ± 0.01	0.17 ± 0.00	0.47 ± 0.21	0.68 ± 0.09	0.46 ± 0.23	1.35 ± 0.88
	nonanal	1.97 ± 0.01	2.84 ± 0.05	2.17 ± 0.02	1.96 ± 0.00	2.61 ± 0.29	2.26 ± 0.23	5.23 ± 2.31
Σ		6.60	198.28	9.44	10.67	22.69	14.35	78.46
Alkenals	2-E-nonenal	0.33 ± 0.02	-	-	-	-	0.40 ± 0.18	0.43 ± 0.22
	2-undecenal	0.74±0.05	-	-	1.88 ± 0.35	1.43 ± 0.12	2.17 ± 0.91	4.71 ± 2.84
Σ		1.07	0.73	-	1.88	1.43	2.57	5.14
Alkadienals	2,4-E,E-dodecadienal	-	0.78^{ab} ± 0.03	0.59^{ab} ± 0.01	0.68^{ab} ± 0.08	0.43^{b} ± 0.01	1.04^{a} ± 0.31	1.11^{a} ± 0.21
	2,4-E,E-decadienal	1.42^{a} ± 0.13	2.20^{ab} ± 0.04	1.14^{a} ± 0.12	1.30^{a} ± 0.45	1.29^{a} ± 0.11	1.66^{a} ± 0.54	3.02^{ab} ± 0.31
Σ		1.42	2.98	1.73	1.98	1.72	2.70	4.13
Acids	pentanoic acid	-	-	0.56^{a} ± 0.04	0.33^{b} ± 0.03	0.51^{a} ± 0.05	-	-
	hexanoic acid	0.74 ± 0.09	1.48 ± 0.25	1.14 ± 0.05	0.49 ± 0.08	0.77 ± 0.13	1.01 ± 0.22	2.57 ± 1.53
	decanedioic acid didecyl ester	-	0.48 ± 0.67	0.92 ± 0.03	0.78 ± 0.05	0.31 ± 0.03	1.39 ± 0.50	0.44 ± 0.06
Σ		0.74	1.96	2.62	1.60	1.59	2.40	3.01
Monoterpenes arom	Limonene	3.50 ± 0.42	1.42^{b} ± 0.13	0.43^{cd} ± 0.01	1.15^{bc} ± 0.30	0.34^{d} ± 0.01	-	-
Sulfide compounds	disulfide bis 1methylethyl	-	1.87^{a} ± 0.18	0.69^{bc} ± 0.02	0.68^{bc} ± 0.13	0.21^{cd} ± 0.01	1.05^{b} ± 0.24	0.29^{cd} ± 0.09
Arom. Hydroc.	ethylbenzene	0.28^{a} ± 0.03	1.93^{b} ± 0.26	0.10^{b} ± 0.00	0.12^{b} ± 0.03	0.07^{b} ± 0.00	0.36^{b} ± 0.12	-
	o-xylene	0.90^{a} ± 0.04	1.76^{b} ± 0.28	0.18^{c} ± 0.00	0.37^{c} ± 0.00	-	-	-
	naphthalene-decahydro-2,3-dimethyl	-	-	0.56 ± 0.02	0.55 ± 0.11	-	-	-
Σ		1.18	3.69	0.84	1.04	0.07	0.36	-

Arom. eterocyclic hydr.	2,5-dimethyl pyrazine	-	-	-	0.25 ± 0.11	0.23 ± 0.02	0.28 ± 0.39	-
	2-pentyl furan	0.58^{ab} ± 0.06	0.81^{a} ± 0.05	0.18^{c} ± 0.01	0.17^{c} ± 0.02	0.18^{c} ± 0.01	0.30^{bc} ± 0.05	0.55^{ab} ± 0.20
Σ		0.58	0.81	0.18	0.42	0.41	0.58	0.55

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.
- under detection limit (<0.01%)

Tab. 3.31- VOCs concentration (ppb) of thermo-oxidized sunflower oil at different treatment times.

THERMO-OXIDIZED SUNFLOWER OIL								
		Time(h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	75.60^{a}±5.63	40.28^{bd}±11.19	33.80^{bc}±0.01	52.64^{d}±1.33	53.62^{d}±3.79	57.60^{d}±3.40	119.24^{e}±66.16
	butyl cyclopentane	-	1.69^{a}±0.39	1.51^{a}±0.13	1.76^{a}±0.15	1.82^{a}±0.13	1.45^{a}±0.11	2.64^{b}±0.2
Σ		75.60	41.97	35.31	54.40	55.44	59.04	121.88
Alkenes	1-octene	-	4.81^{a}±0.98	-	5.25^{a}±0.53	6.01^{a}±0.43	4.50^{a}±0.36	7.87^{b}±0.48
	2-Z-octene	-	2.90^{a}±0.82	1.65^{ab}±0.14	2.90^{a}±0.32	2.29^{ab}±0.16	1.16^{b}±0.04	-
	4-dodecene	-	0.36^{a}±0.15	0.41^{a}±0.05	0.44^{a}±0.01	0.38^{a}±0.03	0.41^{a}±0.00	0.56^{a}±0.04
	2-methyl, 3-ethyl-1,3-hexadiene	-	-	1.98^{a}±0.06	2.26^{a}±0.06	2.46^{a}±0.17	2.41^{a}±0.23	3.14^{b}±0.14
Σ		-	8.07	4.04	10.86	11.14	8.48	11.57
Alcohols	pentanol	-	22.85^{a}±6.26	18.61^{a}±1.31	28.10^{ab}±0.23	28.51^{ab}±2.01	19.35^{a}±1.22	34.49^{b}±1.89
	hexanol	-	1.64^{a}±0.56	1.53^{a}±0.13	1.84^{a}±0.04	1.61^{a}±0.11	1.21^{a}±0.00	2.02^{a}±0.11
	heptanol	-	0.56^{a}±0.16	0.59^{a}±0.06	0.69^{a}±0.06	0.82^{ab}±0.05	0.81^{ab}±0.07	1.00^{b}±0.01
	1-octen-3-ol	-	8.59^{a}±2.74	6.99^{a}±0.13	8.49^{a}±0.04	7.46^{a}±0.53	7.05^{a}±0.19	9.15^{a}±0.35
	octanol	0.16^{a}±0.01	0.33^{a}±0.0	0.61^{a}±0.02	0.40^{a}±0.01	0.62^{a}±0.04	-	1.21^{b}±0.07
Σ		0.16	33.97	28.33	39.52	39.01	28.42	47.88
Alkanals	hexanal	25.30^{a}±1.70	103.99^{b}±34.96	103.06^{b}±4.84	130.15^{bc}±0.58	130.52^{bc}±9.22	128.86^{bc}±25.00	171.42^{c}±3.61
	heptanal	0.92^{a}±0.06	6.36^{b}±1.35	6.64^{b}±0.40	8.16^{b}±0.14	7.86^{b}±0.56	7.58^{b}±1.16	11.80^{c}±0.30
	octanal	1.18^{a}±0.08	2.02^{ab}±0.61	2.15^{ab}±0.16	2.43^{ab}±0.02	3.17^{bc}±0.23	3.85^{bc}±0.81	4.29^{c}±0.40
	nonanal	3.00^{a}±0.20	8.60^{ab}±2.69	8.14^{ab}±0.03	8.47^{ab}±0.01	9.70^{b}±0.69	13.94^{b}±2.58	12.03^{b}±0.29
	decanal	0.19^{a}±0.01	0.36^{abc}±0.15	0.25^{ab}±0.00	0.32^{abc}±0.03	0.44^{abc}±0.03	0.61^{c}±0.08	0.49^{bc}±0.04
	benzhaldehyde	-	0.41^{a}±0.13	0.64^{ab}±0.00	0.75^{b}±0.00	0.64^{ab}±0.04	0.71^{ab}±0.10	0.84^{b}±0.04
Σ		30.58	121.74	120.87	150.29	152.33	155.55	200.87
Alkenals	2-E-hexenal	-	9.47^{a}±3.34	7.68^{a}±0.47	9.06^{a}±0.03	8.46^{a}±0.60	6.89^{a}±0.94	10.24^{a}±0.08
	2-E-octenal	2.42^{a}±0.16	6.98^{b}±2.03	7.47^{b}±0.32	8.69^{b}±0.19	10.64^{b}±0.73	9.69^{b}±1.31	10.88^{b}±0.30
	2-Z-heptenal	2.19^{a}±0.15	43.81^{b}±15.29	39.89^{b}±1.99	42.92^{b}±0.37	38.58^{b}±2.73	34.56^{b}±3.41	46.27^{b}±1.87
	2-E-nonenal	0.29^{a}±0.02	0.99^{b}±0.27	1.54^{c}±0.03	1.79^{cd}±0.01	2.10^{de}±0.15	2.35^{e}±0.02	3.48^{f}±0.09

	2-E-decenal	-	2.99^{a}±0.28	3.53^{a}±0.22	3.64^{a}±0.26	6.65^{b}±0.00	6.15^{b}±0.00	5.57^{b}±3.71
	2-undecenal	0.79^{a}±0.06	2.08^{a}±1.08	2.56^{a}±0.00	2.87^{a}±0.00	5.76^{b}±0.00	6.28^{b}±1.42	4.96^{b}±0.34
Σ		5.69	66.32	62.68	68.96	72.18	65.91	81.40
Alkadienals	2,4-E,E-heptadienal	-	0.62^{a}±0.20	0.34^{a}±0.02	0.45^{a}±0.04	-	-	-
	2,4-E,E-nonadienal	0.33^{a}±0.02	0.37^{ab}±0.09	0.59^{abc}±0.05	0.65^{bc}±0.05	0.90^{d}±0.06	1.07^{d}±0.14	0.84^{cd}±0.01
	2,4-E,E-decadienal	-	18.80^{a}±0.57	19.24^{a}±0.07	18.02^{a}±0.74	22.03^{a}±0.00	20.05^{a}±1.47	21.87^{a}±0.00
Σ		0.33	19.78	20.18	19.12	22.93	21.12	22.71
Ketones	2-heptanone	-	2.09^{a}±0.82	1.88^{a}±0.12	2.71^{a}±0.25	2.81^{a}±0.20	2.36^{a}±0.17	4.24^{b}±0.32
	3-octanone	-	0.29^{a}±0.41	0.54^{a}±0.02	0.72^{a}±0.04	-	-	0.51^{a}±0.72
	cyclodecanone	0.75^{a}±0.06	0.40^{a}±0.00	0.66^{a}±0.00	0.53^{a}±0.68	-	-	-
	2-propylcyclopentanone	8.76^{a}±0.59	0.76^{b}±5.21	-	0.55^{b}±0.75	-	-	1.29^{c}±0.90
	2-cyclohexenone	1.70^{a}±0.11	-	-	0.25^{b}±0.10	2.28a±0.41	1.06^{a}±0.68	0.37^{b}±0.66
	cis-3-hepten-2-one	-	0.67^{a}±0.15	0.60^{a}±0.02	0.67^{a}±0.02	0.80^{a}±0.06	-	0.51^{a}±0.72
Σ		11.21	4.21	3.68	5.42	5.89	3.42	6.92
Acids	octanoic acid	-	0.44^{a}±0.62	-	-	2.36^{b}±0.17	1.57^{b}±0.22	0.89^{a}±0.11
	butanedioic acid methyl bis (1 methylpropyl)ester	-	0.28^{a}±0.12	0.34^{a}±0.00	0.21^{a}±0.40	0.56^{a}±0.05	-	0.44^{a}±0.00
Σ		-	0.71	0.34	0.21	2.92	1.57	1.33
Arom. eterocyclic hydr.	2-butyl furan	-	-	-	2.29^{a}±0.06	2.66^{a}±0.19	1.98^{b}±0.03	3.41^{c}±0.00
	2-pentyl furan	2.01^{a}±0.14	11.92^{b}±3.72	15.11^{bc}±0.89	19.21^{c}±0.02	17.98^{bc}±1.27	15.99^{bc}±0.92	28.71^{d}±1.22
	2-heptyl furan	-	-	-	-	-	-	0.87±0.02
	5-pentyl 2-(3H)-furanone	1.66^{ab}±0.11	-	-	0.48^{a}±0.22	2.39^{c}±0.47	0.73^{a}±0.08	1.92^{bc}±0.25
	2-pyrrolidinone	-	0.51^{abc}±0.13	0.29^{a}±0.01	0.38^{ab}±0.01	0.63^{bcd}±0.05	0.81^{cd}±0.12	0.90^{d}±0.05
	1H-butyl pyrrole	-	-	0.03^{a}±0.00	0.09^{ab}±0.35	0.16^{bc}±0.16	0.20^{c}±0.09	0.24^{c}±0.53
Σ		3.68	12.43	15.43	22.45	23.81	19.70	36.05

a-f: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.32- VOCs concentration (ppb) of frying sunflower oil at different treatment times.

FRYING SUNFLOWER OIL								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	75.60^{abc}±5.	54.16^{a}±7.0	137.11^{bd}±72.	165.12^{d}±71.	197.08^{de}±20.	255.75^{e}±56.	177.44^{d}±13.
	propyl cyclohexane	-	0.86^{a}±0.01	0.23^{bc}±0.03	0.43^{c}±0.20	0.48^{c}±0.12	-	-
	butyl cyclopentane	-	2.28^{a}±0.03	0.90^{bc}±0.02	1.54^{c}±0.37	1.81^{c}±0.11	-	0.24^{b}±0.02
	1-methyl, 2-methylene cyclohexane	-	-	-	-	-	-	0.44±0.03
Σ		75.60	57.30	138.24	167.09	199.37	255.75	178.12
Alkenes	2-Z-octene	-	3.29^{ab}±0.0	4.18^{b}±0.03	1.79^{c}±0.36	2.34^{c}±0.15	-	-
	6-E-dodecene	-	0.49^{a}±0.03	0.26^{a}±0.02	0.37^{a}±0.02	0.38^{a}±0.03	-	-
Σ		-	3.77	4.43	2.16	2.72	-	-
Alcohols	1-pentanol	-	20.52^{ab}±2.	17.78^{b}±2.90	21.13^{a}±0.99	22.88^{a}±5.51	-	-
	1-hexanol	-	3.74^{a}±0.13	0.96^{b}±0.03	1.67^{c}±0.31	1.65^{c}±0.09	-	-
	heptanol	-	-	0.38^{ab}±0.07	0.57^{a}±0.12	0.71^{a}±0.01	0.21^{b}±0.09	0.16^{b}±0.01
	1-octen-3-ol	-	8.71^{a}±0.87	5.18^{b}±1.57	6.55^{b}±0.95	7.79^{a}±0.81	3.04^{c}±1.07	3.01^{c}±0.20
	4-ethyl cyclohexanol	-	1.65^{a}±0.12	0.44^{b}±0.62	1.14^{a}±0.18	1.55^{a}±0.07	-	-
	1-octanol	0.16^{a}±0.01	0.30^{a}±0.06	0.30^{a}±0.16	0.29^{a}±0.04	0.77^{b}±0.19	0.17^{a}±0.11	0.13^{a}±0.01
Σ		0.16	34.91	25.04	31.36	35.34	3.41	3.30
Alkanals	hexanal	25.30^{a}±1.7	115.26^{b}±5.	69.77^{c}±10.9	103.88^{b}±11.	126.72^{b}±6.2	49.40^{ac}±0.9	40.95^{ac}±2.7
	heptanal	0.92^{a}±0.06	7.03^{b}±0.12	3.65^{c}±0.41	6.82^{b}±1.41	7.61^{b}±0.47	1.92^{a}±0.71	1.63^{a}±0.11
	octanal	1.18^{a}±0.08	1.68^{a}±0.04	1.54^{a}±0.45	1.96^{ab}±0.37	2.63^{b}±0.08	1.60^{a}±0.96	1.19^{a}±0.08
	benzhaldehyde	-	0.94^{a}±0.14	0.44^{a}±0.07	0.62^{a}±0.16	0.63^{a}±0.07	-	-
	nonanal	3.00^{a}±0.20	9.15^{b}±0.18	5.87^{c}±1.14	7.27^{bc}±1.18	8.67^{b}±0.65	3.87^{a}±1.49	2.75^{a}±0.18
	decanal	0.19^{a}±0.01	0.23^{a}±0.03	0.26^{ab}±0.04	0.27^{ab}±0.04	0.31^{ab}±0.02	0.19^{a}±0.04	0.13^{a}±0.01
	4-oxononanal	-	1.06^{a}±0.07	1.72^{ab}±0.35	2.17^{bc}±0.56	3.21^{bc}±0.60	0.62^{a}±0.21	0.70^{a}±0.05
Σ		30.58	135.35	83.24	122.99	149.78	57.64	47.35
Alkenals	2-E-hexenal	-	9.40^{a}±0.16	4.56^{b}±0.48	7.38^{a}±1.33	8.10^{a}±0.16	1.32^{c}±0.13	1.26^{c}±0.09
	2-Z-heptenal	2.19^{a}±0.15	48.97^{b}±0.2	24.68^{c}±2.66	34.71^{bc}±5.7	38.48^{b}±0.41	7.89^{ad}±1.66	7.23^{ad}±0.49
	2-E-octenal	2.42^{a}±0.16	7.55^{b}±0.11	4.86^{ac}±0.84	6.67^{b}±1.23	8.01^{b}±0.27	2.68^{a}±0.98	2.04^{a}±0.13
	2-E-nonenal	0.29^{a}±0.02	1.08^{b}±0.04	0.91^{b}±0.14	1.42^{b}±0.13	2.00^{b}±0.16	0.49^{a}±0.16	0.54^{a}±0.03

	2-E-decenal	-	2.43^{a}±0.01	2.95^{a}±0.71	2.96^{a}±0.09	3.85^{ab}±0.37	1.51^{c}±0.51	1.17^{c}±0.08
	2-undecenal	0.79^{a}±0.06	1.30^{b}±0.02	2.86^{bc}±0.88	2.44^{c}±0.31	3.03^{c}±0.20	1.20^{ab}±0.18	0.84^{a}±0.06
Σ		5.69	70.73	40.82	55.58	63.47	15.09	13.07
Alkadienals	2,4-E,E-heptadienal	-	0.87^{a}±0.13	0.31^{ab}±0.03	0.33^{ab}±0.03	0.41^{ab}±0.07	-	-
	2,4-E,E-nonadienal	0.33^{a}±0.02	0.31^{a}±0.01	0.48^{ab}±0.10	0.53^{b}±0.02	0.72^{b}±0.13	0.24^{a}±0.13	0.17^{a}±0.01
	2,4-E,E-decadienal	-	20.73^{a}±1.1	20.90^{a}±3.45	20.26^{a}±1.84	21.95^{a}±1.02	6.00^{b}±0.36	5.30^{b}±0.35
Σ		0.33	21.91	21.69	21.12	23.09±1.22	6.25	5.47
Ketones	2-heptanone	-	2.31^{a}±0.02	1.16^{b}±0.01	2.30^{a}±0.49	2.49^{a}±0.11	0.74^{b}±0.07	0.80^{b}±0.06
	3-octanone	-	0.58^{a}±0.09	0.30^{a}±0.02	0.57^{a}±0.14	0.58^{a}±0.05	-	-
	6-methyl, 2-heptanone		-	-	-	-	-	0.37±0.03
	cyclodecanone	0.75±0.06						
	2-propyl cyclopentanone	8.76±0.59						
	2-cyclohexenone	1.70±0.11						
Σ			2.89	1.45	2.87	3.08	0.74	1.17
Acids	pentanoic acid	-		-	-	-	-	0.28±0.02
	butanedioic acid methyl bis (1-methylpropyl) ester	-	0.19^{a}±0.02	0.46^{ab}±0.07	0.37^{ab}±0.11	0.50^{ab}±0.24	0.40^{ab}±0.08	-
Σ		-	0.19	0.46	0.37	0.50	0.40	0.28
Eterocyclic hydr.	2-butyil furan	-	-	-	1.88^{a}±0.36	2.28^{b}±0.02	-	-
	2-pentyl furan	2.01^{a}±0.14	13.10^{b}±1.0	8.04^{bc}±1.14	16.02^{b}±2.84	18.57^{b}±0.05	4.10^{a}±0.84	3.60^{a}±0.24
	2-pyrrolidinone	-	0.26^{a}±0.05	0.23^{a}±0.08	0.29^{a}±0.06	0.37^{a}±0.14	0.16^{a}±0.07	0.16^{a}±0.01
	5-pentyl 2-(3H)-furanone	1.66^{a}±0.11	0.45^{b}±0.08	1.03^{a}±0.42	0.87^{ab}±0.02	1.18^{a}±0.20	0.54^{b}±0.01	0.38^{b}±0.03
	1H-pyrazolo	-	0.06^{a}±0.01	0.51^{b}±0.25	0.22^{b}±0.18	0.36^{b}±0.25	0.28^{b}±0.13	-
Σ		3.68	13.87	9.81	19.29	22.76	5.08	4.14

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.33- VOCs concentration (ppb) of sunflower oil extracted from French fries at different treatment times.

SUNFLOWER OIL EXTRACTED FROM FRENCH FRIES								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	nonane	-	0.17^{a}±0.03	0.19^{a}±0.02	5.43^{b}±0.82	5.84^{b}±1.30	1.38^{c}±0.02	1.62^{c}±0.11
	decane	-	0.62^{a}±0.19	1.06^{a}±0.07	2.12^{b}±0.04	0.75^{a}±0.17	0.82^{a}±0.23	1.66^{b}±0.12
	dodecane	0.81^{ab}±0.06	0.50^{a}±0.17	0.34^{a}±0.02	1.82^{c}±0.07	0.67^{a}±0.05	1.49^{c}±0.31	1.26^{bc}±0.08
	2,6-dimethyl undecane	0.18^{a}±0.08	-	-	0.09^{a}±0.01	-	-	-
Σ		0.99	1.29	1.59	9.46	7.26	3.69	4.54
Alkenes	1-methyl 4-(1-methylethyl)-1,4-cyclohexadiene	-	0.31±0.13	0.28±0.02	0.27±0.02	0.56±0.11	0.67±0.09	0.46±0.03
Alkanals	hexanal	4.44^{a}±0.33	5.21^{a}±2.20	13.43^{b}±0.99	9.72^{b}±1.34	-	-	4.19^{ac}±0.31
	heptanal	-	0.14^{a}±0.01	0.75^{b}±0.05	-	-	-	-
	octanal	-	0.22^{a}±0.07	0.62^{b}±0.05	0.26^{a}±0.07	0.52^{ab}±0.03	0.66^{b}±0.19	0.79^{b}±0.06
	nonanal	1.97^{ab}±0.08	0.84^{c}±0.31	1.38^{ac}±0.10	1.11^{c}±0.21	2.02^{ab}±0.07	1.87^{ab}±0.07	2.19^{b}±0.15
	decanal	0.15^{ab}±0.01	0.08^{b}±0.02	0.12^{ab}±0.01	0.12^{ab}±0.04	0.16^{a}±0.01	0.20^{a}±0.02	0.20^{a}±0.02
Σ		6.56	6.48	16.31	11.21	2.70	2.72	7.37
Alkenals	2-E-hexenal	-	0.05^{a}±0.01	0.21^{b}±0.01	-	-	-	-
	2-Z-heptenal	-	0.50^{a}±0.19	1.62^{b}±0.12	0.81^{ac}±0.10	1.46^{bc}±0.32	1.42^{bc}±0.09	1.22^{bc}±0.08
	2-E-octenal	-	0.35^{ab}±0.18	0.82^{bc}±0.05	0.87^{bcd}±0.12	1.44^{d}±0.22	1.11^{cd}±0.01	3.43^{e}±0.25
	2-E-nonenal	0.33^{a}±0.02	0.21^{a}±0.09	0.22^{a}±0.01	0.38^{a}±0.06	0.33^{a}±0.00	0.31^{a}±0.04	0.37^{a}±0.03
	2-E-decenal	0.88^{a}±0.06	0.57^{a}±0.24	0.68^{a}±0.05	0.84^{a}±0.32	1.11^{a}±0.02	0.54^{a}±0.77	1.39^{a}±0.11
	2-undecenal	0.74^{ab}±0.05	0.62^{a}±0.21	0.67^{a}±0.04	0.83^{ab}±0.24	1.11^{ab}±0.17	1.33^{bc}±0.08	1.78^{c}±0.13
Σ		1.95	2.31	4.23	3.74	5.45	4.71	8.20
Alkadienals	2,4-E,E-nonadienal	-	0.11^{ab}±0.06	0.10^{a}±0.01	0.12^{ab}±0.02	0.24^{c}±0.02	0.22^{bc}±0.03	0.21^{abc}±0.01
	2,4-E,E-decadienal	1.42^{a}±0.13	6.87^{b}±2.22	5.50^{b}±0.37	4.52^{ab}±0.54	5.94^{b}±0.47	4.95^{ab}±0.69	5.82^{b}±0.43
Σ		1.42	6.99±2.27	5.61	4.65	6.18	5.17	6.04
Ketones	2-propilciclopentanone	-	-	-	0.26^{a}±0.37	0.58^{a}±0.27	0.72^{a}±0.22	-
Σ		-	-	-	0.26	0.58	0.72	-
Acids	hexanoic acid	0.74^{ab}±0.09	0.73^{ab}±0.45	1.19^{abc}±0.08	2.23^{bc}±1.01	2.16^{bc}±0.25	2.54^{c}±0.08	-
	butanedioic acid methyl bis (1-methylpropyl) ester	0.35^{ab}±0.03	0.05^{a}±0.07	-	0.26^{a}±0.20	0.26^{a}±0.14	0.32^{ab}±0.46	1.07^{b}±0.08

Σ		1.09	0.78	1.19	2.49	2.42	2.86	1.07
Arom. eterocyclic hydroc.	methylpyrazine	-	0.05^{a}±0.07	0.37^{b}±0.03	-	-	-	-
	2,5-dimethyl pyrazine	-	0.30^{ab}±0.10	0.50^{b}±0.04	0.41^{ab}±0.09	0.96^{c}±0.14	1.18^{c}±0.20	-
	ethyl pyrazine	-	0.07^{a}±0.09	-	-	-	0.18^{a}±0.26	-
	2-pentyl furan	0.58^{ab}±0.06	0.48^{a}±0.17	1.05^{abcd}±0.08	0.87^{abc}±0.03	1.13^{bcd}±0.30	1.28^{cd}±0.16	1.63^{d}±0.12
	5-pentyl-2-(3H)-furanone	-	0.17^{a}±0.07	0.23^{a}±0.02	0.22^{a}±0.09	0.39^{a}±0.14	0.26^{a}±0.36	-
	2-acetyl-1,4,5,6-tetrahydropyridine	-	0.16±0.02	0.53±0.04	0.38±0.14	0.60±0.85	0.74±1.05	2.04±0.15
Σ		0.58	1.21	2.68	1.89	3.08	3.64	3.66
Arom. Hydrocarbons	*p*-xylene	0.90^{ac}±0.04	0.25^{bd}±0.05	0.96^{abc}±0.07	1.19^{ab}±0.24	0.65^{c}±0.14	0.57^{c}±0.05	-
	1,3,5-trimethyl benzene	-	0.03^{a}±0.00	0.10^{b}±0.02	0.21^{c}±0.01	-	-	-
	1-methyl, 2-(1-methylethyl)-benzene	-	0.10^{a}±0.02	0.14^{b}±0.01	0.19^{c}±0.01	-	-	-
	styrene	2.45±0.16	-	-	-	-	-	-
Σ		3.35	0.38	1.20	1.59	0.65	0.57	-
Monoterpenes arom.	limonene	3.50^{a}±0.42	2.82^{a}±1.08	2.49^{a}±0.19	2.02^{a}±0.12	3.07^{a}±0.82	5.90^{b}±0.24	3.78^{b}±0.26
Σ		3.50	2.82	2.49	2.02	3.07	5.90	3.78

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.34- VOCs concentration (ppb) of thermo-oxidized lard at different treatment times.

THERMO-OXIDIZED LARD								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	$17.88^{a}\pm1.21$	$37.42^{b}\pm2.51$	$43.41^{b}\pm3.23$	$40.35^{b}\pm2.71$	$13.76^{a}\pm0.93$	$17.18^{a}\pm1.16$	$19.46^{a}\pm1.31$
	octane	$0.39^{a}\pm0.03$	$2.25^{b}\pm0.17$	-	$1.55^{c}\pm0.12$	$0.66^{a}\pm0.04$	-	-
	butyl cyclopentane	-	$0.12^{a}\pm0.01$	-	$0.10^{a}\pm0.01$	$0.22^{b}\pm0.01$	$0.07^{c}\pm0.00$	$0.06^{c}\pm0.01$
Σ		18.27	39.79	43.41	42.00	14.64	17.25	19.51
Alcohols	1-octen-3-ol	-	$0.21^{a}\pm0.02$	$0.28^{b}\pm0.02$	$0.17^{ac}\pm0.01$	$0.19^{a}\pm0.02$	$0.12^{cd}\pm0.01$	$0.07^{d}\pm0.01$
	1-octanol	$0.04^{a}\pm0.00$	$0.05^{b}\pm0.00$	-	-	-	-	-
Σ		0.04	0.26	0.28	0.17	0.19	0.12	0.07
Alkanals	hexanal	$2.03^{a}\pm0.13$	$7.46^{bc}\pm0.50$	$13.62^{d}\pm1.01$	$12.03^{de}\pm0.81$	$17.94^{f}\pm1.33$	$10.37^{be}\pm0.70$	$7.11^{c}\pm0.48$
	heptanal	$0.22^{a}\pm0.02$	$0.72^{b}\pm0.05$	$1.03^{c}\pm0.08$	$0.75^{b}\pm0.05$	$0.97^{c}\pm0.07$	$0.50^{d}\pm0.03$	$0.43^{d}\pm0.03$
	octanal	$0.22^{a}\pm0.02$	$0.30^{ab}\pm0.02$	$0.74^{c}\pm0.05$	$0.41^{b}\pm0.03$	$0.66^{c}\pm0.05$	$0.24^{a}\pm0.01$	$0.22^{a}\pm0.01$
	nonanal	$0.52^{ab}\pm0.04$	$0.67^{a}\pm0.04$	$1.38^{c}\pm0.10$	$0.93^{d}\pm0.05$	$1.09^{d}\pm0.08$	$0.40^{b}\pm0.03$	$0.35^{b}\pm0.02$
	decanal	$0.04^{a}\pm0.00$	$0.07^{b}\pm0.01$	$0.10^{c}\pm0.01$	$0.07^{b}\pm0.00$	$0.03^{a}\pm0.00$	$0.03^{a}\pm0.00$	$0.01^{d}\pm0.00$
Σ		3.02	9.22	16.87	14.19	20.70	11.53	8.12
Alkenals	2-E-hexenal	-	$0.29^{a}\pm0.02$	$0.31^{a}\pm0.02$	$0.31^{a}\pm0.02$	$0.26^{ab}\pm0.02$	$0.20^{bc}\pm0.01$	$0.14^{c}\pm0.00$
	2-E-heptenal	$0.16^{a}\pm0.02$	$1.24^{b}\pm0.08$	$1.51^{b}\pm0.11$	$1.27^{b}\pm0.09$	$1.34^{b}\pm0.10$	$0.86^{c}\pm0.06$	$0.65^{c}\pm0.04$
	2-E-ottenal	$0.10^{a}\pm0.01$	$0.21^{bc}\pm0.01$	$0.37^{d}\pm0.03$	$0.23^{bc}\pm0.02$	$0.25^{b}\pm0.02$	$0.17^{ce}\pm0.01$	$0.12^{ae}\pm0.01$
	2-E-decenal	$0.16^{ab}\pm0.01$	$0.21^{ac}\pm0.01$	$0.51^{d}\pm0.03$	$0.26^{c}\pm0.02$	$0.09^{be}\pm0.01$	$0.14^{b}\pm0.01$	$0.04^{e}\pm0.00$
	2-undecenal	$0.13^{ab}\pm0.00$	$0.15^{ac}\pm0.00$	$0.51^{d}\pm0.03$	$0.20^{c}\pm0.01$	$0.03^{e}\pm0.00$	$0.08^{be}\pm0.00$	$0.04^{e}\pm0.01$
Σ		0.55	2.10	3.22	2.27	1.98	1.44	1.00
Alkadienals	2,4-E,E-heptadienal	-	$0.12^{a}\pm0.01$	$0.12^{a}\pm0.01$	$0.05^{b}\pm0.01$	-	$0.03^{b}\pm0.00$	-
	2,4-EE-decadienal	$0.13^{a}\pm0.01$	$0.41^{b}\pm0.03$	$0.84^{c}\pm0.06$	$0.27^{d}\pm0.02$	$0.13^{a}\pm0.01$	$0.12^{a}\pm0.01$	$0.09^{a}\pm0.01$
Σ		0.13	0.52	0.97	0.31	0.13	0.14	0.09
Ketones	2-heptanone	$0.04^{a}\pm0.00$	$0.16^{bc}\pm0.02$	$0.19^{b}\pm0.01$	$0.19^{b}\pm0.01$	$0.27^{d}\pm0.02$	$0.19^{b}\pm0.01$	$0.11^{c}\pm0.01$
	3-octanone	-	$0.02^{a}\pm0.00$	-	$0.03^{b}\pm0.00$	-	$0.02^{a}\pm0.00$	$0.02^{a}\pm0.00$
Σ		0.04	0.18	0.19	0.22	0.27	0.21	0.14

Arom. eterocyclic hydroc.	2-pentyl furan	0.09^{a}±0.01	0.18^{b}±0.01	0.36^{c}±0.03	0.25^{b}±0.02	0.44^{d}±0.03	0.21^{b}±0.01	0.17^{ab}±0.01
Monoterpenes arom.	limonene	0.48^{a}±0.04	0.02^{bc}±0.00	0.06^{b}±0.01	0.02^{bc}±0.00	-	0.01^{bc}±0.00	0.01^{bc}±0.00

a-e: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.35- VOCs concentration (ppb) of frying lard at different treatment times.

FRYING LARD								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	17.88^{a}±1.21	-	30.45^{b}±2.26	3.38^{c}±0.22	27.84^{b}±2.07	-	3.80^{c}±0.28
	octane	0.39^{a}±0.03	-	-	1.97^{b}±0.14	2.74^{c}±0.19	3.19^{c}±0.24	-
	butyl cyclopentane	-	0.13^{a}±0.01	0.11^{a}±0.00	0.09^{a}±0.01	0.11^{a}±0.01	0.08^{a}±0.02	0.08^{a}±0.01
	decane	-	0.06^{a}±0.00	0.05^{a}±0.01	0.04^{a}±0.01	0.05^{a}±0.01	0.06^{a}±0.01	0.05^{a}±0.00
Σ		18.27	0.18	30.61	5.49	30.74	3.34	3.93
Alkanals	hexanal	2.03^{a}±0.13	7.35^{b}±0.54	7.45^{b}±0.55	3.97^{c}±0.27	4.32^{c}±0.29	11.26^{d}±0.84	5.59^{bc}±0.37
	heptanal	0.22^{a}±0.02	0.68^{b}±0.05	0.72^{b}±0.05	0.33^{ac}±0.02	0.73^{b}±0.06	0.61^{bd}±0.04	0.49^{cd}±0.03
	octanal	0.22^{a}±0.02	0.37^{b}±0.03	0.39^{b}±0.03	0.24^{a}±0.02	0.34^{b}±0.03	0.24^{a}±0.01	0.22^{a}±0.02
	nonanal	0.52^{a}±0.04	0.81^{b}±0.08	0.73^{bc}±0.05	0.46^{a}±0.03	0.59^{ac}±0.04	0.62^{abc}±0.05	0.47^{a}±0.04
	decanal	0.04^{ab}±0.00	0.05^{a}±0.01	0.03^{bc}±0.01	0.01^{d}±0.00	0.02^{cd}±0.00	0.02^{cd}±0.00	0.02^{cd}±0.00
Σ		3.02	9.26	9.32	5.00	6.01	12.75	6.79
Alkenals	2-E-hexenal	-	0.18^{a}±0.01	0.14^{ab}±0.01	0.07^{b}±0.00	0.15^{ab}±0.01	0.58^{c}±0.04	0.10^{ab}±0.04
	2-E-heptenal	0.16^{a}±0.02	1.01^{b}±0.07	0.88^{bc}±0.06	0.47^{d}±0.04	0.70^{ce}±0.05	0.67^{e}±0.05	0.39^{d}±0.03
	2-E-octenal	0.10^{ab}±0.01	0.17^{c}±0.02	0.10^{ab}±0.00	0.07^{a}±0.01	0.11^{ab}±0.01	0.13^{bc}±0.02	0.10^{ab}±0.00
	2-E-decenal	0.16^{a}±0.01	0.18^{a}±0.02	0.05^{bc}±0.01	0.04^{b}±0.01	0.08^{bcd}±0.00	0.09^{cd}±0.01	0.11^{d}±0.02
	2-E-undecenal	0.13±0.00	-	-	-	-	-	-
Σ		0.55	1.53	1.18	0.66	1.04	1.46	0.69
Alkadienals	2,4-E,E-decadienal	0.13 ±0.01	-	-	-	-	-	-
Ketones	2-heptanone	0.04^{a}±0.00	0.11^{bc}±0.01	0.10^{b}±0.01	0.05^{a}±0.01	0.15^{c}±0.01	0.19^{d}±0.01	0.10^{b}±0.02
Arom. eterocyclic hydroc.	2-pentyl furano	0.09^{a}±0.01	0.17^{bc}±0.01	0.16^{b}±0.01	0.06^{a}±0.01	0.24^{d}±0.02	0.26^{d}±0.02	0.22^{cd}±0.02
Monoterpenes arom.	limonene	0.48±0.04	-	-	-	-	-	-

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.36- VOCs concentration (ppb) of lard extracted from French fries at different treatment times.

LARD EXTRACTED FROM FRENCH FRIES								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	ethyl cyclohexane	-	0.05^{a}±0.01	0.08^{ab}±0.00	0.09^{b}±0.02	-	-	-
	nonane	-	0.07^{a}±0.01	-	-	0.05^{a}±0.00	-	0.35^{b}±0.03
	dodecane	0.81^{a}±0.06	1.17^{b}±0.09	0.38^{c}±0.03	0.50^{c}±0.03	0.43^{c}±0.03	0.18^{d}±0.02	0.05^{d}±0.01
	tridecane	-	0.80^{a}±0.06	0.50^{b}±0.04	0.56^{b}±0.04	-	0.17^{c}±0.02	-
	heptyl cyclohexane	-	0.33^{a}±0.03	0.19^{b}±0.01	0.17^{b}±0.01	-	-	-
	2,6,11-trimethyl dodecane	-	0.09^{a}±0.01	0.09^{a}±0.01	0.04^{b}±0.00	0.06^{b}±0.01	-	-
	tetradecane	-	0.44^{a}±0.03	0.40^{a}±0.03	0.27^{b}±0.02	0.19^{c}±0.02	-	-
	pentadecane	-	0.22^{a}±0.01	0.49^{b}±0.04	0.14^{c}±0.01	0.08^{c}±0.01	-	-
	hexadecane	-	0.05^{a}±0.01	0.19^{b}±0.01	0.04^{ac}±0.00	0.02^{c}±0.00	-	-
	2,6-dimethyl undecane	0.18^{a}±0.08	0.62^{b}±0.04	0.14^{c}±0.02	0.18^{a}±0.02	0.17^{a}±0.01	0.14^{c}±0.01	-
	hesyl cyclohexane	-	0.36a±0.02	0.11b±0.01	0.12b±0.01	0.12±0.01	-	-
	1,1-dimethyl cyclohexane	-	0.12^{a}±0.01	0.05^{bc}±0.01	0.07^{b}±0.00	0.04^{c}±0.00	-	-
	2-isopropyl 1,3-dimethyl cyclopentane	-	0.33^{a}±0.01	0.06^{b}±0.01	0.17^{c}±0.01	0.14^{c}±0.01	-	-
	1-methyl, 2-pentyl cyclohexane	-	0.23^{a}±0.01	0.08^{bc}±0.01	0.09^{b}±0.00	0.06^{c}±0.01	-	-
	cis decalyn 2-syn methyl	-	0.28^{a}±0.02	0.05^{b}±0.01	0.07^{b}±0.00	0.06^{b}±0.01	-	-
	decalyn syn 1-methyl cis	-	0.13^{a}±0.01	0.03^{b}±0.00	0.03^{b}±0.00	0.02^{b}±0.00	-	-
	cis, cis-1,6-dimethylspiro-(4.5)-decane	-	0.10^{a}±0.01	0.02^{b}±0.00	0.04^{c}±0.00	0.03^{bc}±0.00	-	-
Σ		-	5.39	2.87	2.58	1.45	0.49	0.40
Alkanals	hexanal	4.44±0.33	-	-	-	-	-	-
	heptanal	-	-	0.14^{a}±0.00	0.11^{b}±0.01	-	0.21^{c}±0.02	-
	octanal	-	-	0.14^{a}±0.00	0.12^{a}±0.01	-	0.43^{b}±0.03	0.08^{a}±0.02
	nonanal	1.97^{a}±0.08	0.14^{b}±0.01	0.23^{b}±0.01	0.28^{bc}±0.02	0.38^{cd}±0.03	0.49^{d}±0.03	0.14^{b}±0.01
	decanal	0.15±0.01	-	-	-	-	-	-
Σ		6.56	0.14	0.51	0.51	0.38	1.13	0.22
Alkenals	2-Z-heptenal	-	0.04^{a}±0.01	0.08^{b}±0.01	0.08^{b}±0.00	-	-	-

	2-E-octenal	-	0.05^{a}±0.01	0.07^{a}±0.00	0.08^{ab}±0.01	0.09^{b}±0.01	0.14^{c}±0.01	-
	2-E-nonenal	0.33^{a}±0.02	0.05^{b}±0.01	0.02^{c}±0.00	0.08^{bd}±0.01	0.10^{d}±0.01	0.07^{bd}±0.01	-
	2-E-decenal	0.88^{a}±0.06	-	-	-	-	0.22^{b}±0.01	0.08^{c}±0.00
	2-undecenal	0.74^{a}±0.05	-	-	-	0.18^{b}±0.01	0.08^{c}±0.02	0.07^{c}±0.03
Σ		1.95	0.15	0.17	0.23	0.37	0.51	0.15
Alkadienals	2,4-E,E-decadienal	1.42^{a}±0.13	-	0.30^{bc}±0.02	0.34^{bc}±0.02	0.38^{b}±0.03	0.13^{cd}±0.01	0.23^{bc}±0.02
Acids	pentanoic acid	-	0.09^{a}±0.02	-	0.09^{a}±0.01	0.21^{b}±0.01	0.10^{a}±0.01	-
	hexanoic acid	0.74^{a}±0.09	-	-	0.18^{bc}±0.02	0.27^{b}±0.02	0.06^{c}±0.00	-
	butanedioic acid methyl bis (1-methylpropyl) ester	0.35±0.03	-	-	-	-	-	-
Σ		1.09	0.09	-	0.27	0.48	0.16	-
Arom. eterocyclic hydr.	2,5-dimethyl pyrazine	-	0.12^{a}±0.01	0.20^{b}±0.01	0.24^{b}±0.02	0.49^{c}±0.04	0.27^{d}±0.02	-
	ethyl pyrazine	-	0.02^{a}±0.02	0.06^{b}±0.01	0.08^{b}±0.01	-	-	-
	2-pentyl furan	0.58^{a}±0.06	-	0.07^{bc}±0.01	0.04^{bc}±0.02	-	0.11^{c}±0.01	-
	2-ethyl, 5-methyl pyrazine	-	-	0.08^{a}±0.01	0.09^{a}±0.01	0.34^{b}±0.03	-	-
	3-ethyl 2,5-dimethyl pyrazine	-	0.06^{ab}±0.01	0.03^{ab}±0.00	0.04^{ab}±0.01	0.08^{b}±0.01	0.09^{b}±0.05	-
Σ		0.58	0.20	0.43	0.49	0.91	0.48	-
Arom. hydroc.	ethylbenzene	-	0.09^{ab}±0.01	0.14^{a}±0.01	0.11^{ab}±0.00	0.03^{c}±0.00	0.05^{bc}±0.00	0.02^{c}±0.00
	o-xylene	0.90^{a}±0.04	0.16^{b}±0.01	0.17^{b}±0.01	0.20^{b}±0.02	0.04^{c}±0.00	0.07^{c}±0.00	-
	styrene	2.45^{a}±0.16	0.02^{b}±0.00	-	0.05^{b}±0.00	-	-	0.04^{b}±0.00
	2-methyl decahydro naphthalene	-	0.06^{a}±0.01	0.02^{b}±0.00	0.02^{b}±0.00	0.03^{b}±0.00	-	-
	1,6-dimethyl decahydro naphthalene	-	0.14^{a}±0.01	0.04^{b}±0.00	0.06^{b}±0.01	0.06^{b}±0.01	-	-
Σ		3.35	0.48	0.37	0.44	0.15	0.12	0.06
Monoterpenes arom.	limonene	3.50^{a}±0.42	0.05^{b}±0.01	0.05^{b}±0.01	0.09^{b}±0.01	0.18^{b}±0.01	0.09^{b}±0.02	0.02^{b}±0.00
Sulfide compounds	disulfide bis (1-methyl ethyl)	-	0.14^{a}±0.01	0.06^{b}±0.01	0.06^{b}±0.01	0.05^{b}±0.01	0.04^{b}±0.00	-

a-c: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.37- VOCs concentration (ppb) of thermo-oxidized mix oil at different treatment times.

THERMO-OXIDIZED MIX OIL								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	octane	0.02^{a}±0.00	13.33^{b}±0.90	25.95^{c}±1.74	27.78^{c}±2.06	22.69^{c}±1.53	21.92^{c}±1.63	23.50^{c}±1.58
	propyl cyclohexane	0.01a±0.00	0.07^{b}±0.01	0.15^{c}±0.00	0.16^{c}±0.02	0.14^{c}±0.00	0.16^{c}±0.01	0.17^{c}±0.01
	butyl cyclopentane	-	0.33^{a}±0.02	0.62^{b}±0.04	0.72^{b}±0.06	0.61^{b}±0.04	0.64^{b}±0.04	0.69^{b}±0.05
	4-propyl cyclohexene	-	0.07^{a}±0.01	0.13^{a}±0.01	0.13^{a}±0.01	0.05^{a}±0.07	0.06^{a}±0.01	0.10^{a}±0.01
	docosane	-	0.01^{a}±0.00	0.02^{b}±0.00	0.01^{a}±0.00	0.01^{a}±0.00	-	0.01^{a}±0.00
Σ		0.03	13.82	26.86	28.80	23.50	22.78	24.47
Alkenes	2-Z-octene	-	0.74^{a}±0.03	1.80^{bc}±0.05	2.03^{b}±0.06	0.60^{c}±0.04	0.72^{bc}±0.05	0.74^{bc}±0.05
	4,4-dimethyl 2-E-pentene	-	0.08^{a}±0.01	-	0.14^{b}±0.01	0.12^{b}±0.01	-	-
Σ		-	0.83±0.06	1.81	2.18	0.72	0.72	0.74
Alcohol	1-pentanol	-	-	2.41^{ab}±0.17	2.52^{ab}±0.18	2.15^{b}±0.15	2.33^{ab}±0.16	2.76^{a}±0.19
	1-hexanol	-	-	0.16^{a}±0.02	0.18^{a}±0.01	0.17^{a}±0.01	0.17a±0.01	0.19^{a}±0.02
	1-heptanol	-	0.04^{a}±0.00	0.18^{b}±0.02	0.21^{b}±0.02	0.18^{b}±0.01	0.19b±0.01	0.33^{c}±0.00
	1-octen-3-ol	-	0.16^{a}±0.02	0.35^{b}±0.02	0.39^{b}±0.03	0.40^{b}±0.03	0.43bc±0.03	0.53^{c}±0.04
	1-octanol	-	0.04^{a}±0.01	0.14^{b}±0.01	0.14^{b}±0.01	0.18^{cd}±0.01	0.16bc±0.01	0.21^{d}±0.01
	1-pentadecanol	-	-	-	-	0.02^{a}±0.00	0.01^{a}±0.00	0.03^{b}±0.00
	decanol	-	-	-	-	0.03^{a}±0.00	0.01^{b}±0.00	-
Σ		-	0.24	3.24	3.45	3.13	3.31	4.05
Alkanals	hexanal	0.62^{a}±0.04	-	-	-	0.61^{a}±0.04	0.54^{ab}±0.04	0.49^{b}±0.03
	heptanal	0.04^{a}±0.01	0.77^{b}±0.05	1.60^{c}±0.11	1.63^{c}±0.12	1.56^{c}±0.11	1.63^{c}±0.12	1.86^{c}±0.13
	octanal	0.04^{a}±0.00	0.25^{b}±0.02	0.60^{c}±0.03	0.65^{c}±0.04	0.64^{c}±0.05	0.66^{c}±0.04	0.88^{d}±0.06
	nonanal	14.12^{a}±1.62	1.60^{b}±0.14	3.01^{b}±0.22	2.92^{b}±0.22	2.73^{b}±0.19	2.52^{b}±0.17	3.07^{b}±0.21
	decanal	0.03^{a}±0.00	0.05^{ab}±0.01	0.08^{cd}±0.00	0.09^{c}±0.00	0.06^{bcd}±0.01	0.05^{abd}±0.01	0.07^{bcd}±0.01
	4-oxononanal	-	-	0.11^{a}±0.01	0.10^{a}±0.01	0.23^{b}±0.02	0.22^{b}±0.06	0.30^{b}±0.02
Σ		14.86	2.66	5.39	5.40	5.83	5.63	6.66
Alkenals	2-E-hexenal	-	0.35^{a}±0.02	0.74^{b}±0.05	0.77^{b}±0.05	0.73^{b}±0.05	0.79^{b}±0.06	0.83^{b}±0.06

	2-Z-heptenal	-	1.57^{a}±0.12	-	-	-	2.94b±0.22	-
	2-E-heptenal	0.04^{a}±0.01	0.07^{a}±0.01	3.04^{b}±0.23	3.11^{b}±0.23	2.67^{b}±0.20	-	3.27^{b}±0.24
	2-E-octenal	-	0.27^{a}±0.02	0.63^{b}±0.05	0.66^{b}±0.04	0.65^{b}±0.05	0.66^{b}±0.05	0.79^{b}±0.06
	2-E-nonenal	-	0.04^{a}±0.01	0.17^{b}±0.01	0.20^{bc}±0.01	0.25^{c}±0.02	0.25^{c}±0.03	0.34^{d}±0.02
	2-E-decenal	-	0.25^{a}±0.02	0.71^{b}±0.05	0.77^{b}±0.05	1.04^{b}±0.08	1.04^{b}±0.24	1.09^{b}±0.07
	2-undecenal	-	0.11^{a}±0.01	0.38^{b}±0.03	0.44b±0.03	0.81^{c}±0.06	0.62^{d}±0.04	0.68^{cd}±0.05
Σ		0.04	2.66	5.67	5.95	6.14	6.29	7.00
Alkadienals	2,4-E,E-heptadienal	-	1.47^{a}±0.10	2.44^{b}±0.18	1.74^{a}±0.12	1.65a±0.12	1.50^{a}±0.10	1.74^{a}±0.12
	2,4-E,E-nonadienal	-	-	-	-	0.03^{a}±0.00	-	0.03^{a}±0.00
	2,4-E,E-decadienal	-	0.51^{a}±0.03	1.19^{b}±0.08	0.84^{c}±0.05	1.36^{b}±0.10	0.87^{c}±0.06	0.93^{c}±0.06
Σ		-	1.97	3.63	2.58	3.04	2.37	2.69
Ketones	2-heptanone	-	0.14^{a}±0.01	0.26^{b}±0.02	0.31^{bc}±0.02	0.30^{bc}±0.02	0.37^{cd}±0.03	0.42^{d}±0.03
	3-octanone	-	-	-	-	0.04^{a}±0.00	0.05^{ab}±0.01	0.07^{b}±0.01
	7-methyl, 3-octen-2-one	-	-	0.03^{a}±0.00	-	0.05^{b}±0.01	0.03^{a}±0.00	0.06^{b}±0.01
Σ		-	0.14	0.29	0.31	0.40	0.45	0.55
Arom. eterocyclic hydroc.	2-pentyl furan	-	0.28^{a}±0.02	0.69^{b}±0.05	0.73^{b}±0.05	0.72^{b}±0.05	0.73^{b}±0.05	1.00^{c}±0.07
	2,5-dihydrofuran	-	-	0.01^{a}±0.00	-	-	0.03^{b}±0.00	0.06^{c}±0.01
Σ		-	0.28	0.71	0.73	0.72	0.76	1.06

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.38- VOCs concentration (ppb) of frying mix oil at different treatment times.

FRYING MIX OIL								
		Time(h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	heptane	-	2.76^{ab}±0.21	1.85^{ac}±0.12	3.61^{b}±0.27	0.96^{c}±0.07	11.52^{d}±0.86	1.73^{ac}±0.12
	octane	0.02^{a}±0.00	4.30^{b}±0.29	4.80^{b}±0.35	3.68^{b}±0.28	3.96^{b}±0.27	6.83^{c}±0.51	-
	propyl cycloesane	0.01^{a}±0.00	0.03^{b}±0.00	0.03^{b}±0.00	0.02^{c}±0.00	0.02^{c}±0.00	0.04^{d}±0.00	0.02^{c}±0.00
	butyl cyclopentane	-	0.12^{ab}±0.01	0.12^{ab}±0.01	0.09^{c}±0.01	0.09^{c}±0.00	0.13^{a}±0.01	0.11^{bc}±0.01
	4-propyl cyclohexene	-	0.02^{a}±0.00	0.01^{b}±0.00	0.01^{b}±0.00	0.01^{b}±0.00	0.01^{b}±0.00	-
Σ		0.03	7.22	6.82	7.40	5.04	18.53	1.86
Alcohols	1-pentanol	-	0.48^{a}±0.04	0.30^{b}±0.02	0.02^{c}±0.00	0.32^{b}±0.02	0.35^{b}±0.02	0.13^{d}±0.00
	1-octanol	-	0.11^{ab}±0.01	0.13^{b}±0.01	0.12^{ab}±0.01	0.10a±0.00	0.18^{c}±0.02	0.11^{ab}±0.01
	1-hexanol	-	0.05^{a}±0.00	0.05^{a}±0.01	0.03^{b}±0.00	0.03^{ab}±0.00	0.10^{c}±0.01	0.05^{a}±0.01
	1-heptanol	-	0.03^{ab}±0.00	0.06^{ac}±0.01	0.03^{b}±0.00	0.05^{abc}±0.01	0.08^{c}±0.00	0.05^{abc}±0.01
	1-octen-3-ol	-	0.10^{ab}±0.01	0.11^{ac}±0.00	0.09^{ab}±0.01	0.11^{abc}±0.00	0.12^{c}±0.01	0.08^{b}±0.01
	1-octanol	-	0.03^{a}±0.00	0.03^{a}±0.00	0.02^{a}±0.00	0.03^{a}±0.00	0.05^{b}±0.01	0.03^{a}±0.00
	2-propylen-decan-1-ol	-	-	-	-	-	-	0.01±0.00
Σ		-	0.79	0.68	0.31	0.64	0.87	0.47
Alkanals	hexanal	0.62^{a}±0.04	0.08^{b}±0.01	0.13^{b}±0.01	0.07^{b}±0.00	4.01^{c}±0.27	6.99^{d}±0.52	5.00^{c}±0.34
	heptanal	0.04^{a}±0.01	0.31^{bc}±0.02	0.38^{bd}±0.03	0.25^{c}±0.01	0.33^{bc}±0.02	0.46^{d}±0.04	0.34^{b}±0.02
	octanal	0.04^{a}±0.00	0.22^{bc}±0.01	0.26^{b}±0.02	0.16^{c}±0.02	0.24^{b}±0.01	0.35^{d}±0.03	0.22^{bc}±0.01
	nonanal	14.12^{a}±1.62	0.75^{b}±0.05	0.83^{b}±0.06	0.50^{b}±0.03	0.72^{b}±0.05	1.02^{b}±0.08	0.61^{b}±0.04
	decanal	0.03^{a}±0.00	0.01^{bd}±0.00	0.02^{bc}±0.00	0.01^{d}±0.00	0.02^{c}±0.00	0.05^{e}±0.00	0.02^{c}±0.00
	4-oxononanal	-	0.05^{ab}±0.00	0.04^{abc}±0.00	0.04^{ac}±0.00	0.06^{b}±0.01	0.09^{d}±0.01	0.02^{c}±0.00
Σ		14.86	1.43	1.66	1.02	5.39	8.96	6.22
Alkenals	2-E-hexenal	-	0.14^{a}±0.01	0.16^{ab}±0.01	0.12^{a}±0.01	0.13^{a}±0.01	0.19^{b}±0.02	0.13^{a}±0.01
	2-Z-heptenal	-	0.93^{a}±0.06	0.91^{a}±0.07	0.63^{b}±0.04	0.75^{ab}±0.05	0.93^{a}±0.07	0.60^{b}±0.04
	2-E-heptenal	0.04^{ab}±0.01	0.05^{ab}±0.01	0.06^{b}±0.01	0.03^{a}±0.00	0.04^{ab}±0.01	0.05^{ab}±0.00	0.03^{a}±0.00
	2-E-octenal	-	0.20^{a}±0.01	0.20^{a}±0.01	0.15^{b}±0.01	0.18^{ab}±0.01	0.22^{a}±0.01	0.14^{b}±0.01

	2-E-nonenal	-	0.04^{ab}±0.00	0.04^{ab}±0.00	0.03^{a}±0.00	0.05^{b}±0.01	0.07^{c}±0.01	0.04^{ab}±0.00
	2-E-decenal	-	0.32^{ab}±0.02	0.30^{ab}±0.02	0.20^{c}±0.01	0.27^{a}±0.02	0.36^{b}±0.02	0.14^{c}±0.01
	2-undecenal	-	0.22^{ab}±0.02	0.18^{ac}±0.01	0.16^{c}±0.02	0.20^{abc}±0.02	0.25^{b}±0.02	0.08^{d}±0.01
Σ		0.04	1.91	1.86	1.32	1.63	2.08	1.17
Alkadienals	2,4-E,E-heptadienal	-	0.22^{a}±0.01	0.70^{b}±0.05	0.39^{c}±0.03	0.42^{cd}±0.03	0.51^{d}±0.03	0.21^{a}±0.02
	2,4-E,-nonadienal	-	0.01^{a}±0.00	-	-	0.01^{a}±0.00	0.01^{a}±0.00	-
	2,4-E,E-decadienal	-	0.93^{a}±0.07	0.56^{b}±0.03	0.40^{c}±0.03	0.45^{bc}±0.03	0.53^{bc}±0.04	0.17^{d}±0.01
Σ		-	1.16	1.25	0.79	0.88	1.04	0.38
Ketones	cyclohexanone	-	0.05^{a}±0.01	0.04^{ab}±0.00	0.03^{bc}±0.00	0.03^{bc}±0.00	0.05^{a}±0.00	0.02^{c}±0.00
	2-heptanone	-	0.08^{ac}±0.01	0.10^{ab}±0.01	0.06^{c}±0.01	0.08^{ac}±0.00	0.11^{b}±0.01	0.09^{ab}±0.01
	3-octanone	-	-	-	0.03^{a}±0.00	0.01^{b}±0.00	0.03^{a}±0.00	0.01^{b}±0.00
	7-methyl, 3-octen-2-one	-	0.01^{a}±0.00	-	-	0.01^{a}±0.00	0.01^{a}±0.00	-
Σ		-	0.13	0.14	0.12	0.13	0.20	0.12
Arom. eterocyclic. hydroc.	2-pentyl furan	-	0.08^{a}±0.01	0.13^{ab}±0.01	0.12^{a}±0.05	0.13^{ab}±0.01	0.20^{bc}±0.02	0.23^{c}±0.01

a-d: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.39- VOCs concentration (ppb) of mix oil extracted from French fries at different treatment times.

MIX OIL EXTRACTED FROM FRENCH FRIES								
		Time (h)						
Compounds (ppb)		**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	pentyl cyclopropane	-	-	0.18^{a}±0.01	0.09^{b}±0.01	0.05^{c}±0.01	-	-
	5,6-dimethyl decane	-	-	-	-	-	0.04^{a}±0.01	0.02^{b}±0.01
	2,6-dimethyl undecane	0.18±0.08	-	-	-	-	-	-
	octane	-	0.06^{a}±0.01	0.18^{b}±0.01	0.16^{b}±0.02	0.09^{a}±0.01	0.16^{b}±0.02	-
	3-methyloctane	-	-	0.11^{a}±0.01	0.09^{b}±0.00	0.05^{c}±0.01	-	0.06^{bc}±0.01
	1-ethyl, 2-methyl-cis-cyclohexane	-	0.07^{a}±0.01	0.11^{b}±0.00	0.08^{a}±0.01	0.04^{c}±0.00	0.04^{c}±0.01	-
	trans-1,2-diethyl cyclopentane	-	-	-	-	0.04^{a}±0.00	0.05^{b}±0.01	-
	nonane	-	0.12^{a}±0.01	0.25^{b}±0.02	0.19^{ab}±0.02	0.12^{a}±0.00	-	0.14^{a}±0.01
	decane	-	0.03^{a}±0.00	0.03^{ab}±0.00	0.02^{bc}±0.00	0.02^{c}±0.00	-	0.02^{c}±0.00
	2,2,4,6,6-pentamethyl heptane	-	0.08^{a}±0.01	0.10^{b}±0.01	0.08^{a}±0.01	0.07^{a}±0.01	0.04^{c}±0.01	0.07^{a}±0.01
	dodecane	0.81^{ab}±0.06	0.59^{c}±0.04	0.60^{c}±0.05	0.88^{a}±0.06	0.98^{a}±0.06	0.63^{bc}±0.04	0.78^{abc}±0.05
	tridecane	-	0.02^{a}±0.00	0.03^{b}±0.00	0.02^{a}±0.00	0.03^{ab}±0.00	0.01^{c}±0.01	0.04^{b}±0.01
Σ		0.99	0.98	1.59	1.60	1.49	0.98	1.13
Alkenes	1-octene	-	-	0.07^{a}±0.00	0.07^{a}±0.01	0.02^{b}±0.00	-	-
Σ		-	-	0.07	0.07	0.02	-	-
Alcohols	2,2-dimethyl, 1-pentanol	-	-	-	0.05^{a}±0.00	0.04^{b}±0.00	-	-
	isobutyl alcohol	-	-	0.08^{a}±0.01	0.04^{b}±0.00	-	0.08^{a}±0.01	0.05^{ab}±0.01
	2,4-dimethyl, 1-heptanol	-	-	0.04^{a}±0.00	-	0.02^{b}±0.00	0.05^{a}±0.01	-
Σ		-	-	0.12	0.09	0.06	0.12	0.05
Alkanals	hexanal	4.44^{a}±0.03	-	-	-	-	-	-
	octanal	-	0.10^{a}±0.01	0.08^{ab}±0.01	0.06^{abc}±0.00	0.06^{c}±0.00	0.09^{abc}±0.01	0.05^{bc}±0.01
	nonanal	1.97^{a}±0.08	0.12^{b}±0.01	0.16^{b}±0.01	0.10^{b}±0.01	0.12^{b}±0.01	0.22^{b}±0.02	0.12^{b}±0.01
	decanal	0.15^{a}±0.01	0.01^{b}±0.00	0.02^{bc}±0.00	0.01^{b}±0.00	0.02^{bc}±0.00	0.03^{c}±0.01	0.02^{bc}±0.00
Σ		6.56	0.23	0.26	0.18	0.19	0.35	0.19
Alkenals	2-Z-heptenal	-	0.06^{ab}±0.01	0.08^{a}±0.01	0.06^{ab}±0.01	0.04^{b}±0.00	0.08^{a}±0.01	0.06^{ab}±0.01

	2-E-nonenal	0.33^{a}±0.02	0.07^{b}±0.01	0.09^{b}±0.00	0.06^{b}±0.01	0.07^{b}±0.01	0.06^{b}±0.01	0.10^{b}±0.01
	2-E-decenal	0.88^{a}±0.06	0.06^{bc}±0.01	0.10^{bc}±0.00	0.09^{bc}±0.00	0.08^{bc}±0.00	0.12^{c}±0.01	0.13^{b}±0.03
	2-undecenal	0.74^{a}±0.05	0.07^{b}±0.01	0.12^{b}±0.01	0.11^{b}±0.01	0.10^{b}±0.01	0.14^{b}±0.01	0.13^{b}±0.01
Σ		1.95	0.27	0.38	0.32	0.28	0.39	0.41
Alkadienals	2,4-decadienal	1.42^{a}±0.13	0.21^{b}±0.02	0.24^{b}±0.02	0.22^{b}±0.02	0.14^{b}±0.00	0.20^{b}±0.02	0.16^{b}±0.02
Σ		1.42	0.21	0.24	0.22	0.14	0.20	0.16
Ketones	4-methyl cycloheptanone	-	0.04^{a}±0.00	0.09^{b}±0.00	0.06^{c}±0.00	0.03^{a}±0.00	-	-
Σ		-	0.04	0.09	0.06	0.03	-	-
Acids	hexanoic acid	0.74^{a}±0.09	-	-	-	-	0.06^{b}±0.01	0.06^{b}±0.01
	butanedioic acid methyl bis (1-methylpropyl) ester	0.35±0.33	-	-	-	-	-	-
Σ		1.09	-	-	-	-	0.06	0.06
Arom. eterocyclic Hydr.	2(3H)- dihydro furanone	-	-	0.04^{a}±0.00	0.03^{b}±0.00	-	0.01^{c}±0.01	0.02^{d}±0.01
Σ		-	-	0.04	0.03	-	0.01	0.02
Arom. Hydr.	ethylbenzene	-	0.03^{a}±0.00	0.10^{b}±0.01	0.08^{b}±0.01	0.05^{b}±0.01	0.08^{b}±0.01	0.06^{b}±0.01
	styrene	2.45±0.16	-	-	-	-	-	-
	p-xylene	-	0.21^{ac}±0.02	0.31^{b}±0.02	0.28^{ab}±0.02	0.17^{c}±0.02	0.05^{d}±0.01	0.19^{c}±0.02
	o-xylene	0.90^{a}±0.04	0.06^{b}±0.00	0.12^{cd}±0.01	0.09^{c}±0.01	0.07^{b}±0.01	0.13^{d}±0.01	0.06^{b}±0.01
	1-ethyl, 3-methyl benzene	-	-	0.07^{a}±0.01	0.05^{b}±0.01	0.04^{b}±0.00	-	0.04^{b}±0.01
	1,2,3-trimethyl benzene	-	0.06^{abc}±0.00	0.08^{a}±0.00	0.06^{ab}±0.00	0.06^{bc}±0.00	0.01^{d}±0.00	0.05^{c}±0.02
	1-methyl, 3-propyl benzene	-	0.03^{a}±0.00	-	0.03^{a}±0.00	0.03^{a}±0.00	-	0.04^{b}±0.01
	1-methyl, 2-(1-methylethyl)benzene	-	0.04^{ab}±0.01	0.07^{c}±0.01	0.05^{ac}±0.01	0.04^{ab}±0.00	0.02^{b}±0.00	0.05^{ac}±0.01
	1-ethyl 2,3-dimethyl benzene	-	0.05^{a}±0.01	0.09b±0.01	0.04^{a}±0.00	0.07^{c}±0.00	-	0.08^{bc}±0.01
	2-methyl decahydro naphthalene	-	0.06^{a}±0.01	-	-	0.05^{a}±0.01	-	0.06^{a}±0.02
	1,2,4,5-tetramethyl benzene	-	0.03^{ab}±0.00	0.04^{a}±0.00	0.02^{c}±0.00	0.02^{bc}±0.01	-	0.02^{bc}±0.01
Σ		3.35	0.58	0.87	0.72	0.60	0.29	0.66
Arom. Monoterpenes	limonene	3.50^{a}±0.42	0.08^{b}±0.01	0.06^{b}±0.01	0.11^{b}±0.01	0.11^{b}±0.01	0.09^{b}±0.01	0.08^{b}±0.02
Σ		-	0.08	0.06	0.11	0.11	0.09	0.08

a-c: Different letters indicate significant differences ($p \leq 0,05$) between treatment times.

- under detection limit (<0.01%)

Tab. 3.40- Percentage content of different classes of VOCs in thermo-oxidized bi-fractionated palm oil, at different treatment times.

THERMO-OXIDIZED BI-FRACTIONATED PALM OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	20.67	1.87	2.22	2.78	2.45	2.99	2.74
Alkenes	-	0.31	0.24	-	-	1.62	1.80
Alcohols	-	3.90	3.00	3.87	6.05	5.76	1.91
Alkanals	79.33	60.38	61.77	60.62	60.43	58.14	62.34
Alkenals	-	16.10	15.29	13.18	12.04	10.04	10.98
Alkadienals	-	2.85	3.01	2.03	1.45	0.76	0.82
Ketons	-	1.74	1.44	1.41	1.09	1.11	1.48
Acids	-	5.52	0.16	0.13	0.55	0.10	0.05
Aromatic eterocyclic Hydrocarbons	-	4.05	4.82	6.31	4.84	3.66	5.24
Ethers	-	-	0.17	0.18	0.11	0.09	0.10

Tab. 3.41- Percentage content of different classes of VOCs in frying bi-fractionated palm oil, at different treatment times.

FRYING BI-FRACTIONATED PALM OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	20.67	20.56	24.02	29.62	17.51	25.46	26.48
Alkenes	-	1.32	1.00	1.21	1.70	1.84	1.54
Alcohols	-	4.64	4.57	4.59	4.73	3.74	3.64
Alkanals	79.33	53.61	50.96	49.20	53.92	51.63	51.98
Alkenals	-	11.29	12.13	10.48	14.72	11.46	10.93
Alkadienals	-	4.71	3.47	1.92	3.72	2.69	1.99
Ketones	-	0.80	0.90	0.84	0.91	0.89	0.92
Acids	-	0.26	0.17	0.25	0.48	0.22	0.28
Aromatic eterocyclic hydrocarbons	-	2.80	2.78	1.90	2.30	2.08	2.24

Tab. 3.42- Percentage content of different classes of VOCs in bi-fractionated palm oil extracted from French fries, at different treatment times.

BI-FRACTIONATED PALM OIL EXTRACTED FROM FRENCH FRIES							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	5.09	8.36	7.20	3.38	11.13	7.61	7.12
Alkanals	33.74	21.70	14.57	9.43	10.51	11.56	21.11
Alkenals	10.03	11.31	11.27	13.81	16.28	15.08	28.43
Alkadienals	7.30	8.20	10.28	5.50	5.37	5.02	9.96
Ketones	-	1.13	1.34	0.83	2.41	1.31	0.28
Acids	5.61	19.81	21.05	40.36	16.60	14.83	12.79
Aromatic eterocyclic hydrocarbons	2.98	3.48	2.46	1.58	-	-	-
Aromatic hydrocarbons	17.23	12.11	14.04	10.95	20.80	24.98	6.10
Monoterpenes	18.00	13.90	17.79	14.16	16.89	19.60	14.21

Tab. 3.43- Percentage content of different classes of VOCs in thermo-oxidized olive oil, at different treatment times.

THERMO-OXIDIZED OLIVE OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	68.61	47.23	47.76	49.34	48.51	58.54	55.13
Alkenes	-	0.57	0.38	0.26	0.38	0.11	0.12
Alcohols	0.21	5.18	6.14	5.78	4.50	3.71	4.28
Alkanals	24.93	25.09	24.22	25.18	26.41	21.73	24.46
Alkenals	2.61	12.94	13.52	12.29	13.32	10.68	11.27
Alkadienals	-	5.13	3.21	2.67	2.47	2.05	1.29
Ketones	0.62	0.79	1.37	1.15	1.13	0.77	0.95
Acids	1.75	1.58	1.18	1.01	0.85	0.65	0.30
Aromatic eterocyclic hydrocarbons	1.27	1.43	2.14	2.11	2.44	1.69	2.15
Monoterpenes	-	0.06	0.09	0.21	-	0.07	0.04

Tab. 3.44- Percentage content of different classes of VOCs in frying olive oil, at different treatment times.

FRYING OLIVE OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	68.61	47.39	33.44	40.73	33.02	73.77	28.40
Alkenes	-	0.15	0.13	0.08	0.09	0.03	0.00
Alcohols	0.21	0.81	1.19	1.11	1.14	0.51	1.21
Alkanals	24.93	38.19	48.25	45.98	50.73	19.12	54.79
Alkenals	2.61	9.32	11.00	8.63	10.23	4.63	10.53
Alkadienals	-	2.63	3.60	1.83	2.35	1.00	1.75
Ketones	0.62	0.28	0.46	0.43	0.50	0.24	0.60
Acids	1.75	0.81	1.28	0.54	1.00	0.30	1.36
Aromatic eterocyclic hydrocarbons	1.27	0.42	0.65	0.67	0.94	0.41	1.37

Tab. 3.45- Percentage content of different classes of VOCs in olive oil extracted from Frenchf ries, at different treatment times.

OLIVE OIL EXTRACTED FROM FRENCH FRIES							
				Time(h)			
Compounds(%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	5.09	14.53	61.09	63.32	31.39	67.85	18.47
Alkenes	-	1.40	4.58	0.20	0.82	2.15	0.00
Alcohols	-	0.82	4.26	1.48	1.01	1.55	0.54
Alkanali	33.74	78.24	17.81	22.62	56.59	19.29	73.94
Alkenals	10.03	-	-	-	-	-	-
Alkadienals	7.30	1.17	3.26	3.57	4.04	3.49	3.65
Acids	5.61	2.06	7.06	6.18	5.02	4.46	2.92
Aromatic eterocyclic hydrocarbons	2.98	0.32	0.34	0.76	0.96	0.75	0.49
Aromatic hydrocarbons	17.23	1.45	1.58	1.87	0.16	0.47	-
Aromatic Monoterpenes	18.00	-	-	-	-	-	-

Tab. 3.46- Percentage content of different classes of VOCs in thermo-oxidized sunflower oil, at different treatment times.

THERMO-OXIDIZED SUNFLOWER OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	59.41	13.57	12.14	14.65	14.37	16.26	22.97
Alkenes	-	2.61	1.39	2.92	2.89	2.33	2.18
Alcohols	0.13	10.99	9.74	10.65	10.12	7.82	9.02
Alkanals	24.03	39.37	41.56	40.49	39.50	42.83	37.86
Alkenals	4.47	21.45	21.55	18.58	18.72	18.15	15.34
Alkadienals	0,26	6.40	6.94	5.15	5.94	5.81	4.28
Ketones	8.81	1.36	1.27	1.46	1.53	0.94	1.30
Acids	-	0.23	0.12	0.06	0.76	0.43	0.25
Aromatic eterocyclic hydrocarbons	2,89	4.02	5.30	6.05	6.17	5.42	6.79

Tab. 3.47- Percentage content of different classes of VOCs in frying sunflower oil, at different treatment times.

FRYING SUNFLOWER OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	59.41	16.81	42.51	39.52	39.87	74.27	70.27
Alkenes	-	1.11	1.36	0.51	0.54	-	-
Alcohols	0.13	10.24	7.70	7.42	7.07	0.99	1.30
Alkanals	24.03	39.70	25.60	29.09	29.95	16.74	18.68
Alkenals	4.47	20.75	12.55	13.15	12.69	4.38	5.16
Alkadienals	0.26	6.43	6.67	5.00	4.62	1.81	2.16
Ketones	8.81	0.85	0.45	0.68	0.62	0.21	0.46
Acids	-	0.06	0.14	0.09	0.10	0.12	0.11
Aromatic eterocyclic hydrocarbons	2.89	4.07	3.02	4.56	4.55	1.48	1.63
Others	-	-	-	-	-	-	0.23

Tab. 3.48- Percentage content of different classes of VOCs in sunflower oil extracted from French fries, at different treatment times.

SUNFLOWER OIL EXTRACTED FROM FRENCH FRIES							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	5.09	5.74	4.45	25.18	22.71	12.02	12.92
Alkanals	33.74	28.71	45.85	29.83	8.44	8.89	21.00
Alkenals	10.03	10.24	11.89	9.96	17.04	15.36	23.35
Alkadienals	7.30	30.94	15.76	12.36	19.34	16.87	17.20
Ketones	-	-	-	0.70	1.83	2.36	-
Acids	5.61	3.46	3.36	6.62	7.57	9.33	3.04
Aromatic eterocyclic hydrocarbons	2.98	5.36	7.52	5.02	9.64	11.87	10.43
Aromatic hydrocarbons	17.23	3.08	4.16	4.96	3.81	4.03	1.31
Aromatic Monoterpenes	18.00	12.48	7.01	5.38	9.61	19.27	10.76

Tab. 3.49- Percentage content of different classes of VOCs in thermo-oxidized lard, at different treatment times..

THERMO-OXIDIZED LARD							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	80.78	76.12	66.42	70.67	38.19	55.78	67.03
Alcohols	0.17	0.49	0.42	0.29	0.49	0.40	0.25
Alkanals	13.34	17.64	25.81	23.88	53.98	37.28	27.89
Alkenals	2.44	4.02	4.93	3.82	5.15	4.67	3.42
Alkadienals	0.56	1.00	1.48	0.53	0.33	0.47	0.32
Ketones	0.18	0.34	0.29	0.37	0.69	0.69	0.46
Aromatic eterocyclic hydrocarbons	0.42	0.35	0.55	0.42	1.16	0.68	0.58
Aromatic Monoterpenes	2.10	0.04	0.10	0.03	-	0.03	0.04

Tab. 3.50- Percentage content of different classes of VOCs in frying lard, at different treatment times.

FRYING LARD							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	80.78	1.62	73.99	48.77	80.52	18.54	33.49
Alcohols	0.17	-	-	-	-	-	-
Alkanals	13.34	82.21	22.53	44.45	15.73	70.81	57.89
Alkenals	2.44	13.62	2.84	5.87	2.73	8.13	5.92
Alkadienals	0,56	-	-	-	-	-	-
Ketones	0.18	1.02	0.25	0.41	0.39	1.06	0.85
Aromatic eterocyclic hydrocarbons	0.42	1.53	0.39	0.49	0.62	1.46	1.86
Aromatic Monoterpenes	2.10	-	-	-	-	-	-

Tab. 3.51- Percentage content of different classes of VOCs in lard extracted from French fries, at different treatment times.

LARD EXTRACTED FROM FRENCH FRIES							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	5.09	81.25	60.17	51.54	33.36	15.59	37.05
Alkanals	33.74	2.17	10.58	10.10	8.76	35.91	20.60
Alkenals	10.03	2.28	3.57	4.55	8.48	16.11	13.64
Alkadienals	7.30	-	6.35	6.72	8.78	4.25	21.57
Acids	5.61	1.34	0.00	5.45	11.00	5.10	-
Aromatic eterocyclic hydrocarbons	2.98	2.96	9.08	9.87	20.91	15.22	-
Aromatic hydrocarbons	17.23	7.18	7.76	8.78	3.52	3.79	5.52
Aromatic Monoterpenes	18.00	0.68	1.14	1.86	4.13	2.71	1.62
Sulfide compounds	-	2.15	1.33	1.13	1.06	1.32	-

Tab. 3.52- Percentage content of different classes of VOCs in thermo-oxidized mix oil, at different treatment times.

THERMO-OXIDIZED MIX OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	0.20	61.14	56.43	58.31	54.04	53.83	51.82
Alkenes	-	3.67	3.80	4.41	1.66	1.71	1.58
Alcohols	-	1.04	6.80	6.98	7.21	7.82	8.57
Alkanals	99.50	11.77	11.33	10.93	13.42	13.30	14.11
Alkenals	0.30	11.76	11.92	12.04	14.12	14.87	14.82
Alkadienals	-	8.73	7.62	5.22	6.98	5.59	5.70
Ketones	-	0.63	0.62	0.63	0.92	1.07	1.17
Aromatic eterocyclic hydrocarbons	-	1.25	1.48	1.47	1.65	1.80	2.23

Tab. 3.53- Percentage content of different classes of VOCs in frying mix oil, at different treatment times.

FRYING MIX OIL							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	0.20	56.71	54.33	66.84	36.46	58.11	17.83
Alcohols	-	6.24	5.46	2.76	4.61	2.74	4.46
Alkanals	99.50	11.23	13.24	9.19	38.95	28.10	59.53
Alkenals	0.30	15.04	14.84	11.90	11.77	6.52	11.18
Alkadienals	-	9.08	9.98	7.14	6.34	3.27	3.62
Ketones	-	1.05	1.08	1.12	0.91	0.63	1.16
Aromatic eterocyclic hydrocarbons	-	0.65	1.07	1.05	0.97	0.63	2.20

Tab. 3.54-Percentage content of different classes of VOCs in mix oil extracted from French fries, at different treatment times.

MIX OIL EXTRACTED FROM FRENCH FRIES							
	Time (h)						
Compounds (%)	**0**	**8**	**16**	**24**	**32**	**40**	**48**
Alkanes	5.09	40.99	42.55	47.18	51.07	39.38	40.77
Alkenes	-	-	1.97	1.96	0.68	-	-
Alcohols	-	-	3.13	2.70	2.13	4.91	1.93
Alkanals	33.74	9.55	7.06	5.21	6.54	13.90	7.05
Alkenals	10.03	11.30	10.24	9.46	9.62	15.69	14.89
Alkadienals	7.30	8.79	6.39	6.43	4.70	8.13	5.68
Ketones	-	1.59	2.49	1.68	0.97	-	-
Acids	5.61	-	-	-	-	2.23	2.31
Aromatic eterocyclic hydrocarbons	2.98	-	1.05	0.82	-	0.49	0.71
Aromatic hydrocarbons	17.23	24.24	23.40	21.22	20.65	11.51	23.88
Aromatic Monoterpenes	18.00	3.53	1.73	3.35	3.64	3.76	2.77

Tab. 3.55-Trend of Σalkanes and its correlation with TPC in bi-fractionated palm oil samples at different treatment times.

THERMO-OXIDIZED BI-FRACTIONATED PALM OIL	
Time (h)	**Σalkanes**
0	0.93
8	4.56
16	4.51
24	7.02
32	7.15
40	7.61
48	10.50
R^2	**0.8650**

Tab. 3.56- Trend of 2,4-E,E-nonadienal, 2,4-E,E-decadienal, 2,4-E,E-dodecadienal and Σalkadienals and their correlation indices in olive oil samples at different treatment times (thermo-oxidation and frying).

	THERMO-OXIDIZED OLIVE OIL				FRYING OLIVE OIL
Time (h)	**2,4-E,E-nonadienal**	**2,4-E,E-decadienal**	**2,4-E,E-dodecadienal**	**Σalkadienals**	**Σalkadienals**
0	-	-	-	-	-
8	0.70	13.36	4.21	21.08	4.29
16	0.63	9.36	2.88	15.92	3.82
24	0.49	6.56	2.78	11.56	2.83
32	0.41	6.08	2.03	10.18	2.59
40	0.30	4.53	2.00	7.74	1.99
48	0.28	3.81	-	4.95	1.61
R^2	**0.9161**	**0.8349**	**0.8123**	**0.8822**	**0.9490**

Tab. 3.57- Trend of octanal and butyl pyrrole and their correlation indices in thermo-oxidized sunflower oil samples at different treatment times.

	THERMO-OXIDIZED SUNFLOWER OIL	
Time (h)	**octanal**	**butyl pyrrole**
0	1.18	-
8	2.02	-
16	2.15	0.03
24	2.43	0.09
32	3.17	0.16
40	3.85	0.20
48	4.29	0.24
R^2	**0.9499***	**0.9905***

*correlation does not include values at time 0.

Tab. 3.58-Trend of 1-octen-3-ol, octonal, 2-E-nonenal, 2-E-decenal, 2-heptanone, 2-pentyl furan, Σalkenals e Σketones and their correlation indices in thermo-oxidized mix oil samples at different treatment times.

THERMO-OXIDIZED MIX OIL								
TPC	**1-octen-3-ol**	**octanal**	**2-E-nonenal**	**2-E-decenal**	**2-heptanone**	**2-pentyl furan**	**Σalkenals**	**Σketones**
0	-	0.04	-	-	-	-	0.04	-
8	0.16	0.25	0.04	0.25	0.14	0.28	2.66	0.14
16	0.35	0.60	0.17	0.71	0.26	0.69	5.67	0.29
24	0.39	0.65	0.20	0.77	0.31	0.73	5.95	0.31
32	0.40	0.64	0.25	1.04	0.3	0.72	6.14	0.4
40	0.43	0.66	0.25	1.04	0.37	0.73	6.29	0.45
48	0.53	0.88	0.34	1.09	0.42	1.00	7.00	0.55
R^2	**0.6694***	**0.6421***	**0.7407**	**0.5623**	**0.7136***	**0.6368***	**0.4710**	**0.8055***

* correlation does not include values at time 0.

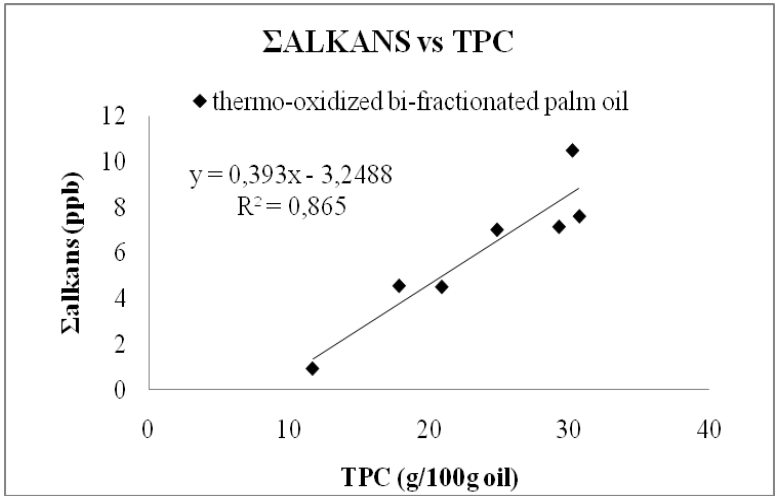

Fig. 3.16-Correlation between TPC and Σalkanes in thermo-oxidized bi-fractionated palm oil.

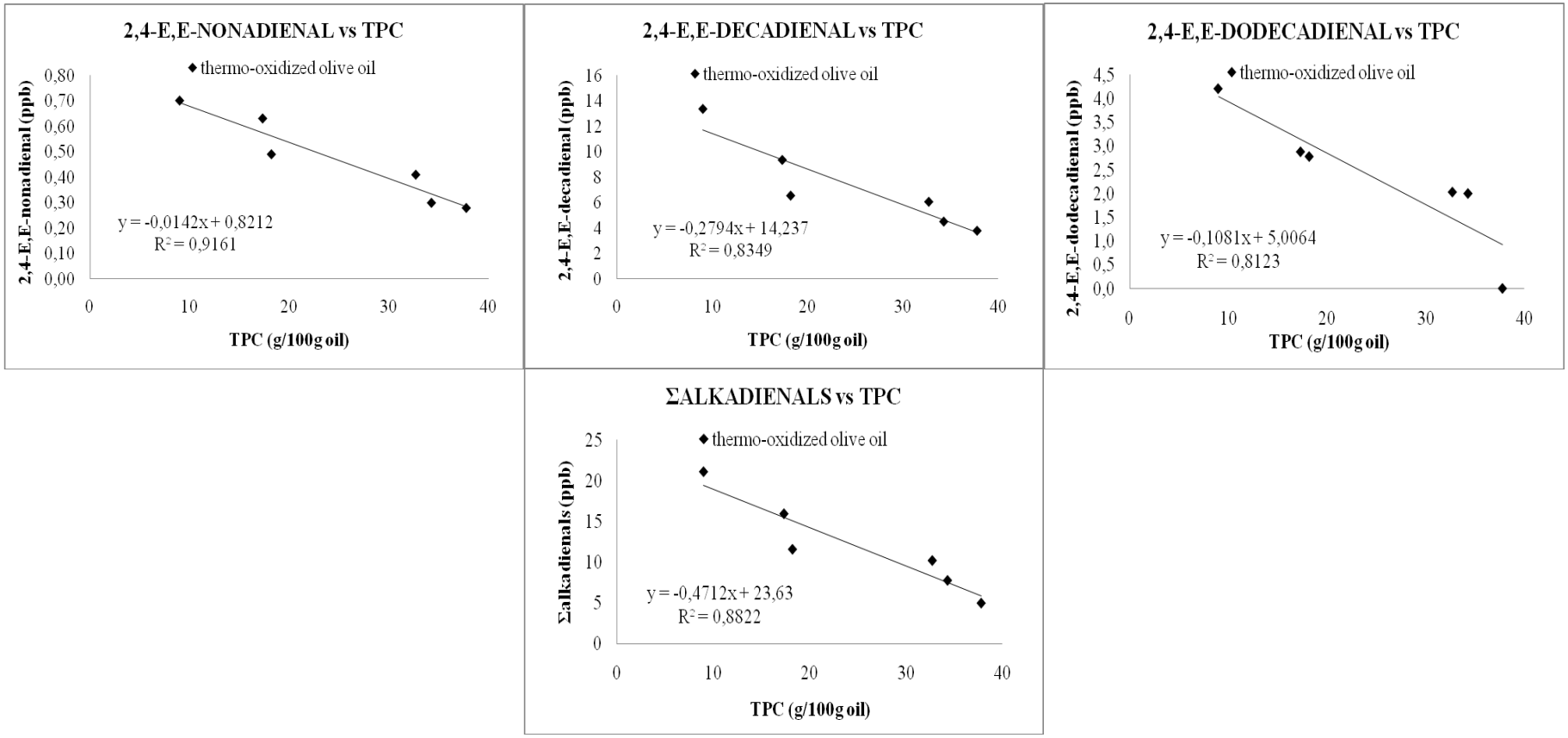

Fig. 3.17-Correlations between TPC and 2,4-E,E-nonadienal, 2,4-E,E-decadienal, 2,4-E,E-dodecadienal and Σalkadienals in thermo-oxidized olive oil samples..

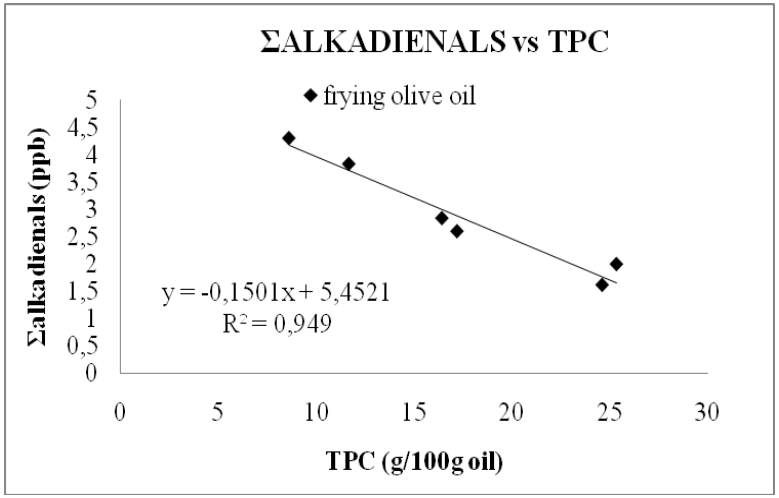

Fig. 3.18-Correlation between TPC and Σalkadienals in frying olive oil samples.

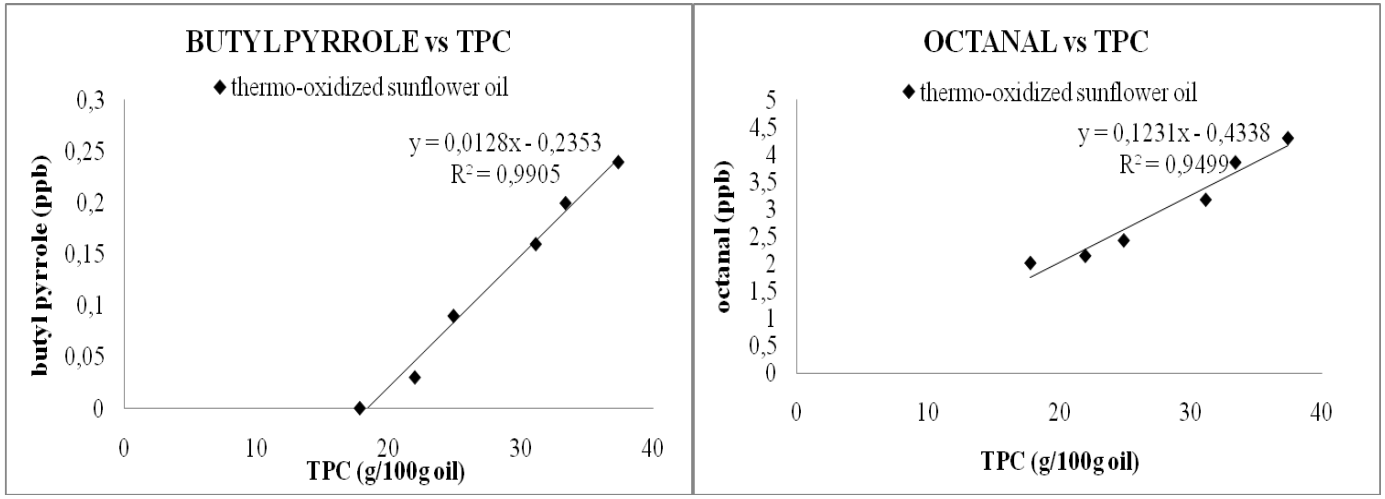

Fig. 3.19-Correlations between TPC and octanal and butyl pyrrole (without values at time 0) in thermo-oxidized sunflower oil samples.

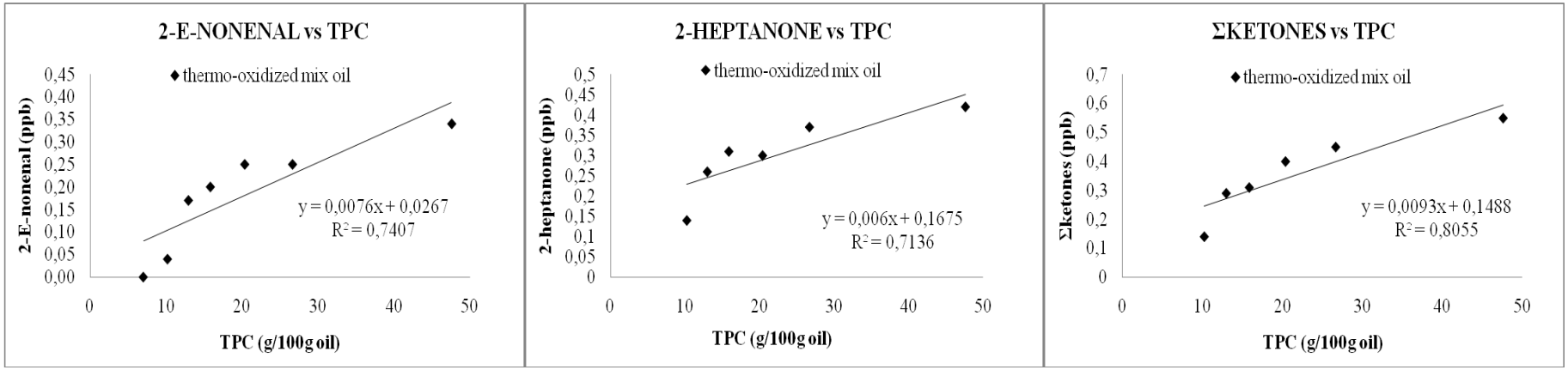

Fig. 3.20-Correlations between TPC and 2-E-nonenal and between TPC and 2-heptanone e Σketones (without values at time 0) in thermo-oxidized mix oil samples.

ABSTRACT

Deep-fat frying is an important, common and highly versatile process, which has been used from antiquity to cook a wide variety of products. During deep-fat frying, hydrolysis, oxidation and polymerization reactions cause a spectrum of physical and chemical changes, leading to the formation of decomposition products posing a direct impact damaging both the oil quality and the fried food nutritional value. The amount and type of degradation products formed in frying oils is primarily dependent on the fatty acid composition of the frying oil, so it is important to keep this in mind in selecting frying oils. Therefore, the choice of medium frying remains of great interest and of crucial importance, not only for its potential nutritional value but also for its ability to withstand the drastic conditions of this cooking technique. The objective of this study was to evaluate the effects of discontinuous and prolonged heat treatment on five oils, characterized by different ratios of unsaturated/saturated fatty acids. In addition, we attempted to identify possible markers of heat treatment correlated with total polar compounds (TPC) in assessing the quality of used frying oils. The determination of TPC has been adopted as a unique official method to test for excessive use of fats for frying. But because there are many variables that affect oil degradation, a specific marker may be ideal for one oil but completely useless in another. In fact, the work wanted to show that it is not correct to use the same indicator for all fatty matrices but, on the basis of the fatty acid composition of the oil or fat used in frying, the indicator that best suits it.
The experimentation was carried out by a prolonged and discontinuous deep-fat frying process with frozen pre-fried potatoes (McCain) and by a simple thermo-oxidation process of oil without food matrix. Both thermal treatments were conducted over a period of 8h per day for 6 days. Every hour, 200 g of frozen pre-fried potatoes were deep fried for 4min (based on preliminary trials). The batch volume of deep fat fryer was 3L. Fresh oil was added every 8h after oil samples were collected, to maintain a constant level in the fryer. The oils used were: bi-fractionated palm oil, olive oil, sunflower oil, lard, and a mix oil. After frying process, the French fries were subjected to fat extraction. Three sets of samples were collected:

- thermo-oxidized oil samples
- frying oil samples
- fat samples extracted from French fries

So, the samples analyzed correspond to following treatment hours: 8, 16, 24, 32, 40, 48 and the oil and French fries samples of time “0”. All samples were subjected to the following determinations:

- free fatty acids (FFA) determination by alkaline titration;
- peroxide value (PV) determination by iodometric titration;
- TPC determination;
- fatty acids (FA) composition determination by gas-chromatographic (GC) analysis of fatty acid methyl esters (FAME);
- volatile organic compounds (VOC) analysis by dynamic head-space system (DHS) coupled with GC and mass spectrometer (MS).
- Statistical analysis.

About performances of three sets of samples (thermo-oxidized, frying and extracted from potatoes), about FFA values, the best fat frying has proved to be the sunflower oil. About PV, during thermo-oxidation process the mix oil, followed by bi-fractionated palm oil, olive oil and sunflower oil, showed the best results while the lard showed the highest values. During frying process the worst oil appeared to be the mix oil and about fats extracted from French fries the worst oil appeared to be the sunflower oil. The sunflower oil appeared to be the best during frying, while about extraction from potatoes, lard was showed to have the lowest values. Considering the performance recorded in three sets of samples, about TPC determination, the best fat turned out to be the frying lard. About changes of fatty acids occurred during the heat treatment possible markers of oil degradation were:
• For the bi-fractionated palm oil C8:0 and Σtrans
• For the olive oil UFA/SFA
• For the sunflower oil C18:2 n6cis, C18:2 n6cis/C16:0 and UFA/SFA
• For lard UFA/SFA
• For the mix oil C8:0
Among VOCs, possible markers could be the Σalkanes for bi-fractionated palm oil, the Σalkadienals for olive oil samples, the octanal and butyl pyrrole for sunflower oil and 2-E-nonenal, 2-heptanone and Σketones for mix oil. The highly variable pattern of VOCs in lard is not allowed to get any good correlation. In conclusion a specific marker may be ideal for one oil but completely useless in another.

RIASSUNTO

La frittura è un processo di cottura molto diffuso ed altamente versatile, usato sin dall'antichità per cucinare un'ampia gamma di prodotti alimentari. Durante la frittura, le reazioni di idrolisi, ossidazione e polimerizzazione causano una serie di cambiamenti fisici e chimici che portano alla formazione di prodotti di degradazione che possono danneggiare sia la qualità dell' olio che il valore nutrizionale dei cibi fritti. La quantità e il tipo di prodotti di degradazione che si formano negli oli di frittura dipendono principalmente dalla composizione in acidi grassi dell' olio di partenza. Pertanto è bene tenere questo a mente nella scelta del mezzo di frittura. Quindi, la scelta del mezzo di frittura è di grande interesse e di fondamentale importanza non solo dal punto di vista nutrizionale ma anche in relazione alla sua capacità di sopportare le drastiche condizioni di questo metodo di cottura. L' obiettivo di questo studio è stato quello di valutare gli effetti di un trattamento termico prolungato e discontinuo su cinque oli, caratterizzati da diversi rapporti di acidi grassi insaturi/saturi (UFA/SFA). Un ulteriore obiettivo è stato quello di riuscire a proporre dei nuovi indicatori di termo-ossidazione da affiancare ai composti polari totali (CPT). La determinazione dei CPT è stata adottata come l' unica procedura ufficiale in grado di stabilire quando il bagno di olio va cambiato. Tuttavia, poiché sono molte le variabili che influenzano la degradazione dell' olio, un indicatore può essere utile per un olio ma completamente inutile in un altro. Infatti, questo studio vuole dimostrare come non sia corretto usare lo stesso indicatore indifferentemente per più matrici grasse ma, a seconda della composizione acidica dell' olio di partenza, scegliere l' indicatore che meglio si adatta. La sperimentazione ha previsto un processo di frittura prolungata e discontinua con patate pre-fritte surgelate e un processo di semplice termo-ossidazione senza alcuna matrice alimentare. Entrambi i processi sono stati condotti per 8h al giorno per 6 giorni. Ogni ora sono state fritte 200g di patate. Al termine di ogni giorno il bagno d' olio (3L) è stato rabboccato con olio fresco per mantenere costante il livello di olio nella friggitrice.

Gli oli usati sono stati: olio di palma bi-frazionato, olio di oliva, olio di girasole, strutto e olio mix. Al termine di ogni ciclo di frittura, le patate sono state sottoposte ad estrazione del grasso. Sono state raccolte tre serie di campioni: termo-ossidati, di frittura ed estratti dalle patate fritte. I campioni analizzati corrispondono alle seguenti ore di trattamento: 8, 16, 24, 32, 40, 48 a cui vanno aggiunti i campioni di olio a tempo 0. Le analisi eseguite sono state:

- determinazione dell' acidità
- determinazione del numero di perossidi (NP)
- determinazione dei CPT
- determinazione della composizione acidica
- determinazione dei composti organici volatili (COV)
- analisi statistica

Considerando le tre serie di campioni, sulla base dei valori di acidità libera, il miglior grasso di frittura si è rivelato essere l' olio di girasole. Per quanto riguarda i risultati relativi al NP, durante il processo di termo-ossidazione i migliori risultati si sono registrati per l' olio mix seguito dall' olio di palma bi-frazionato, dall' olio di oliva e dall' olio di girasole, mentre lo strutto ha mostrato i valori di NP più alti. Durante il processo di frittura l' olio peggiore è stato l' olio mix, mentre per quanto riguarda i grassi estratti dalle patate il peggiore è stato l' olio di girasole. Quest' ultimo ha però mostrato il miglior andamento in frittura mentre lo strutto ha fatto registrare i più bassi valori di NP nei campioni estratti. Relativamente ai CPT, il miglior grasso di frittura, per le tre serie di campioni, è stato lo strutto. Le modificazioni a carico degli acidi grassi durante il trattamento termico hanno permesso di identificare dei nuovi possibili indicatori:

• C8:0 eΣtrans per l' olio di palma bi-frazionato
• UFA/SFA per l' olio di oliva
• C18:2 n6cis, C18:2 n6cis/C16:0 e UFA/SFA per l' olio di girasole
• UFA/SFA per lo strutto
• C8: 0 per l' olio mix

Tra i COV, possibili nuovi indicatori potrebbero essere Σalcani per l' olio di palma bi-frazionato, Σalcadienali per l' olio di oliva, ottanale e butil pirrolo per l' olio di girasole, 2-E-nonenale, 2-eptanone e Σchetoni per l' olio mix. Nello strutto i COV hanno registrato un andamento estremamente variabile, che non ha permesso di ottenere buone correlazioni per nessuno dei volatili identificati. In conclusione si evince quindi che un indicatore che può essere utile nella valutazione di un olio è completamente inutile per un altro.