Review Article

Fatty acid alterations in oils and fats during heating and frying

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Oils and fats degrade during the frying process and many reactions with numerous fatty acid alteration products have been examined. The geometrical isomerisation of double bonds leads to the formation of *trans* fatty acids. At frying temperatures also conjugated double bond systems are detected. The reaction of oxygen with unsaturated fatty acids results in hydroperoxides, which immediately degrade in further radical reactions at frying temperature. A set of oxygenated fatty acids has been detected including epoxy-, keto- and hydroxyl fatty acids. Another route leads to β-scission at the carbonyl- or the alkyl side of the oxygen bearing carbon atom in the fatty acid chain. In this case short chain fatty acids, aldehydic, keto, and hydroxyl acids appear together with volatile compounds. Also the formation of cyclic and furan fatty acids was detected. As a reaction between fatty acids also dimeric and polymerised fatty acids can be observed. Taking into account the different amounts of these fatty acid degradation products the physiological relevance has to be discussed. Due to high concentrations of dimeric and polymerised molecules these substances can lower significantly the digestibility of fried foods, while oxidised fatty acid monomers are readily absorbed and raise concern about their effect on lipid metabolism. These two different effects of altered TAGs and fatty acids have to be considered separately.

Keywords: CFAM / CLA / Frying / TFA / Thermo-oxidation

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1 Introduction

Frying of foods has gained more and more acceptance all over the world although some physiological drawbacks have been recognised for degraded frying fats and fried foods for many years. Nevertheless, the fried products are estimated for their crispy texture, the roasted, fried aroma and their pleasant golden to brown colour. Fats and oils provide effective heat transfer during the frying process, but there is also a mass transfer with a significant uptake of frying oil into the fried good and at the same time loss of moisture, lipids, proteins and carbohydrates from the fried goods. The moisture reduction for potato products starts from about 80% moisture and ends at levels down to 50% [1]. Due to the *Maillard* reaction proteins and carbohydrates form dark brown debris at the bottom of the frying vessel, which has to be filtered off regularly. After frying a significant amount of oil is sucked into the product during the cooling period after the removal from the fryer. Most of the absorbed oil is located in the crust region. This leads to an increase of the oil content of french-fries to about 5 g/100 g oil for pre-fried and 10–15 g/100 g oil in the finished products [1, 2].

Thermoxidative degradation of the fatty acids occurs during long periods of heating and can be perceived by an off-flavour. Abused frying fat is hard to digest and consumption leads to diarrhoea [3]. However, it will be partially digested and taken up into the human body, where it leads to some toxicological concerns [4]. During the past decades the degradation of fats and oils has been investigated extensively. Many reactions take place at the elevated temperatures of about 170–200°C during frying. They can be classified as hydrolysis, isomerisation, oxidation and di- and polymerisation reactions [5]. However, hydrolysis and isomerisation are observed at low levels, only. All these different reactions are influenced by many factors like the frying temperature, composition of the frying media, the ingredients and properties of the fried goods, the presence, composition

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Abbreviations: CFAM, cyclic fatty acids; **CLA,** conjugated fatty acids; **TFA,** trans-fatty acids

and concentration of antioxidants, the time of frying, intermitted or continuous mode of frying, frequency of replenishment and filtration of the frying oil, uptake of frying oil by the fried goods, ratio of the amount of frying oil and surface, the effect of water steam blanket or covering agents like silicone as oxygen barrier and many more [6].

Due to the numerous reactions also a great number of degradation products have been identified such as free fatty acids, partial- and polymerised glycerides, short chain-, trans-, conjugated-, epoxy-, hydroxyl-, keto-, cyclic fatty acids and further reaction products from the decomposition of hydroperoxides like aldehydes, hydroxy aldehydes and hydrocarbons [7]. In addition to the degradation of fatty acids also other minor constituents of the frying fats like sterols [8], tocopherols [9] and others are involved into these reactions, but should be discussed separately. This article gives an overview about the different degradation products of fatty acids reported in frying fats at elevated temperatures such as frying conditions, their analysis procedures, the levels observed in thermoxidised and real frying fats and some aspects about their physiological significance. At first, changes of the double bond configuration and shifting of the double bond position within the fatty acid are discussed. Thereafter the different kinds of changes of single fatty acids are highlighted and at the end polymerisation as a reaction product of at least two fatty acids are focused on.

1.1 *Trans* fatty acids

Trans fatty acids (TFA) are unsaturated fatty acids with at least one or more double bonds in the *trans* position. Most naturally occurring fatty acids double bonds show a *cis* and isolated configuration. However, *trans* double bonds are more stable than *cis* double bonds and result from reactions where sufficient activation energy is provided. In heating experiments the double bond isomerisation was considerably suppressed by the addition of different antioxidants and under nitrogen stream [10]. Also the calculated internal rotational barrier heights of the double bonds in the experiments with oleic and elaidic acid matched well to those of a radical standard substance like 2-butene radical. These results suggest that heat-induced double bond isomerisation is induced by radical species [7, 10]. At higher frying temperatures above 200°C the double bond can also be shifted to adjacent positions when conjugated systems can be formed [11].

Analysis of TFA can be achieved by several procedures. Most often they are determined by GLC of the FAME, which requires a transesterification procedure to convert the natural TAGs into FAME without formation of TFA during sample preparation. In most methods alkaline potassium hydroxide or sodium methanolate in methanol is used as transesterification reagent. After a reaction time of about 1 min with vigorous agitation the reaction is stopped by addition of diluted acid in order to get a stable solution of FAME and to avoid further saponification reactions. For trace amounts of TFA below or at a level of 0.05 g/100 g transesterification procedures using strong acids or TMSH as in ISO method 5509 are not recommended for this special scope, because acids catalysed the formation of TFA or isomerisation [12, 13]. Other analysis techniques use IR spectroscopy like FTIR [14, 15], NIR or Raman spectroscopy [16], ^{1}H-NMR [17] and ^{13}C-NMR [18]. Some differences between TFA contents measured by GC and IR techniques may be observed as conjugated double bonds are to be evaluated separately and in GC chromatograms polymerised species will not be detected. In addition in GC analysis even using polar stationary phases and very long capillaries not all individual *trans* isomers of the FAME can be separated from the *cis* isomers for partially hydrogenated fats [19]. In fried food with long chain PUFA like fish the identification of *trans* isomers by GLC is still a challenge [20, 21]. However, also for IR techniques using Fourier transformation some drawbacks are known determining TFA contents at or even below 2 g/100 g like underlying absorbance, which has to be compensated in order to get accurate results [22, 23].

TFA are only present at trace levels in most vegetable oils and at levels below 2 g/100 g in most refined fats and oils. Fats produced by partially hydrogenation can contain high amounts of up to 40 g/100 g TFA in oils [11]. They occur in low amounts at 3 to 5 g/100 g in dairy and beef fat due to bacterial transformation of unsaturated fatty acids in the rumen of ruminant animals.

Common frying processes at about 170–180°C do not increase the TFA content to a high extent [7, 24–26]. In these studies only an increase at about 1–2 g/100 g was observed even after a long period of frying. However, there are also some publications which noted a significant change of TFA during frying due to the oil exchange between the frying good and the frying media. In practice most French-fries are made from par-fried French-fries. Some of the par-fried products are produced using partially hydrogenated fats with a high content of TFA. The par-fried French-fries contain about 5–6 g/100 g of oil, which is almost totally exchanged during the final frying and leads to an increase of the TFA content in the frying fat. Another contribution studied the increase of TFA depending on the vessel material [27]. Also an effect of antioxidants on formation of TFA was observed, when added to the frying system [26].

High contents of TFA in foods are of concern for human health, because they promote coronary heart disease. An increase of the blood levels of LDL (LDL) cholesterol and TAGs and a decrease of the level of HDL (HDL) cholesterol can be observed. There is further evidence for effects in connection with sudden cardiac death and systemic inflammation [28].

1.2 Conjugated fatty acids

In the same way as elaidic acid is formed from oleic acid also CLA (CLA) is formed from linoleic acid during frying in small amounts. CLA contains two conjugated double bonds,

which can be found between positions 8 to 14 in the carbon chain and can show (*cis*, *cis*), (*cis*, *trans*), (*trans*, *cis*) and (*trans*, *trans*) configuration [29].

At frying temperatures of 180°C after 10 heating cycles for 30 min the CLA content and composition did not rise or change significantly. However, only during heating at high temperatures like 220°C the CLA content increased in refined sunflower oil from 0.1 to 1.3 g/100 g and the CLA isomers (9-*trans*, 11-*trans*) and (10-*trans*, 12-*trans*) with two double bonds in *trans* position were identified as the major isomers. At the same time *cis*/*trans*, *trans*/*cis* isomers can be found at a lower extend [29, 30]. Due to the reaction mechanism in heated oils the identified mono trans CLA isomers comprise (*cis*-9, *trans*-11), (*trans*-9, *cis*-11), (*trans*-10, *cis*-12), (*cis*-10, *trans*-12), (*trans*-8, *cis*-10), and (*cis*-11, *trans*-13) 18:2 acids while (*cis*-8, *trans*-10) and (*trans*-11, *cis*-13) 18:2 isomers were not detected in heated oils containing linoleic acid [31]. The prevalence of CLA isomers with two double bonds in *trans* configuration in heated oils is in contrast to the isomer composition in dairy fats, where the 18:2 *cis*-9, *trans*-11 and 18:2 *trans*-9, *cis*-11 dominate.

Some beneficial physiological effects have been suggested for CLA such as anti-obesity effects, prevention of cardiovascular diseases, cancer preventive effects, bone health effects, immune and inflammatory response effects [32]. However, also negative effects of CLA were observed like increase of oxidative markers, liver functions, milk fat depression, glucose homeostasis [32]. Some of the effects are attributed to single isomers like 18:2 *trans*-10, *cis*-12. Therefor the different isomer compositions of CLA products as they are used as food supplements strongly influence the physiological effects.

There are no reports about the presence of conjugated linolenic acid in heated oils and fats. In spite that linolenic acid is more susceptible to degradation than linoleic acid the conjugated isomers of linolenic acid can not be observed at reasonable amounts in heated oils. This is due to the higher reactivity of conjugated linolenic acid isomers compared to their precursors with isolated double bonds. Enzymatically produced conjugated linolenic isomers have to be used as esterified TAGs in addition with antioxidants in order to ensure a product stable enough to be absorbed before degradation [33].

As a conclusion for the presence of TFA and CLA in frying oils the proper choice of temperature during frying, the selection of frying oils with low TFA content and the use of par-fried products low in TFA will ensure a low overall TFA and CLA content in fried products. Exceeding the recommended temperatures of about 175° will reduce frying times, but increase the formation of TFA and CLA [34].

1.3 Cyclic fatty acids

Fatty acids with more than one double bond in the carbon chain are able to form cycles of five to six ring members during frying and in processes using higher temperatures of 200°C and even above as for deodorisation. Cycles may be closed intramolecularly and intermolecularly with and without hetero atoms [35, 36]. In addition also bicyclic fatty acid monomers were identified in small amounts and mechanisms for the formation of cyclic fatty acid monomers (CFAM) and bicyclic fatty acid monomers (BFAM) [36, 37]. CFAM and BFAM are consumed with the food as contaminants and absorbed from the intestine and metabolised. They were estimated to be highly toxic [38], but a more recent study from Sébédio and co-workers relativised this risk assessment [36, 39]. The content of CFAM in frying oils was reported at levels of about 0.01–0.05 mg/g [36].

The analysis of CFAM starts with a transesterification of oils and fats by alkaline reaction. The non-polar fraction of the FAME is isolated by liquid chromatography on silicic acid followed by urea fractionation. The non-adducted fraction contains CFAM and BFAM and may be further purified by preparative reversed phase HPLC in the recycle mode [40]. In a more recent approach [36] the phenacyl esters of cyclic fatty acids were separated by silver ion HPLC with fractionation according to the degree of unsaturation, the size of the ring and the position and configuration of the double bonds. In a second step these fractions were each examined by GC-MS as their picolinyl ester and 4,4-dimethyloxazolin derivatives.

1.4 Short chain fatty acids

Short chain fatty acids (SCFA) from fatty acid degradation are fatty acids with seven to nine carbon atoms. Caprylic acid is at the same time a common constituent in lauric oils, i.e. palm kernel oil or coconut oil and in dairy fats or medium chain triaclyglycerols (MCT). However, SCFA are also formed in small amounts during the course of the oxidative fatty acid degradation [41]. In a first step oxygen is able to connect to an unsaturated fatty acid. This reaction yields a hydroperoxide, which decomposes rapidly at frying conditions and produces an alkoxy radical. The alkoxy radical can split by homolytic β-scission at each side of the oxygen linked carbon. Figure 1 shows examples for the formation of the different short chain degradation products. If the oxygen linked carbon is split off and a proton is added to the remaining fatty acid chain, this result in a SCFA which remains attached to the glycerol backbone. Thus, SCFA are stable non-volatile products from the thermal decomposition of the fatty acid hydroperoxides [42]. The additionally formed aldehydes are partly evaporated at frying conditions. SCFA consist of a chain length of 7 or 8 carbon atoms depending on the position of the hydroperoxide group in the carbon chain. All the major unsaturated fatty acids (oleic, linoleic and linolenic acid) can form caprylic acid from their 9-hydroperoxides. However, heptanoate is generated exclusively by oleic acid from the 8-hydroperoxides, which are not observed for linoleic and linolenic acid [42].

The SCFA content can be analysed easily together with the composition of fatty acids, which is one of the analyses

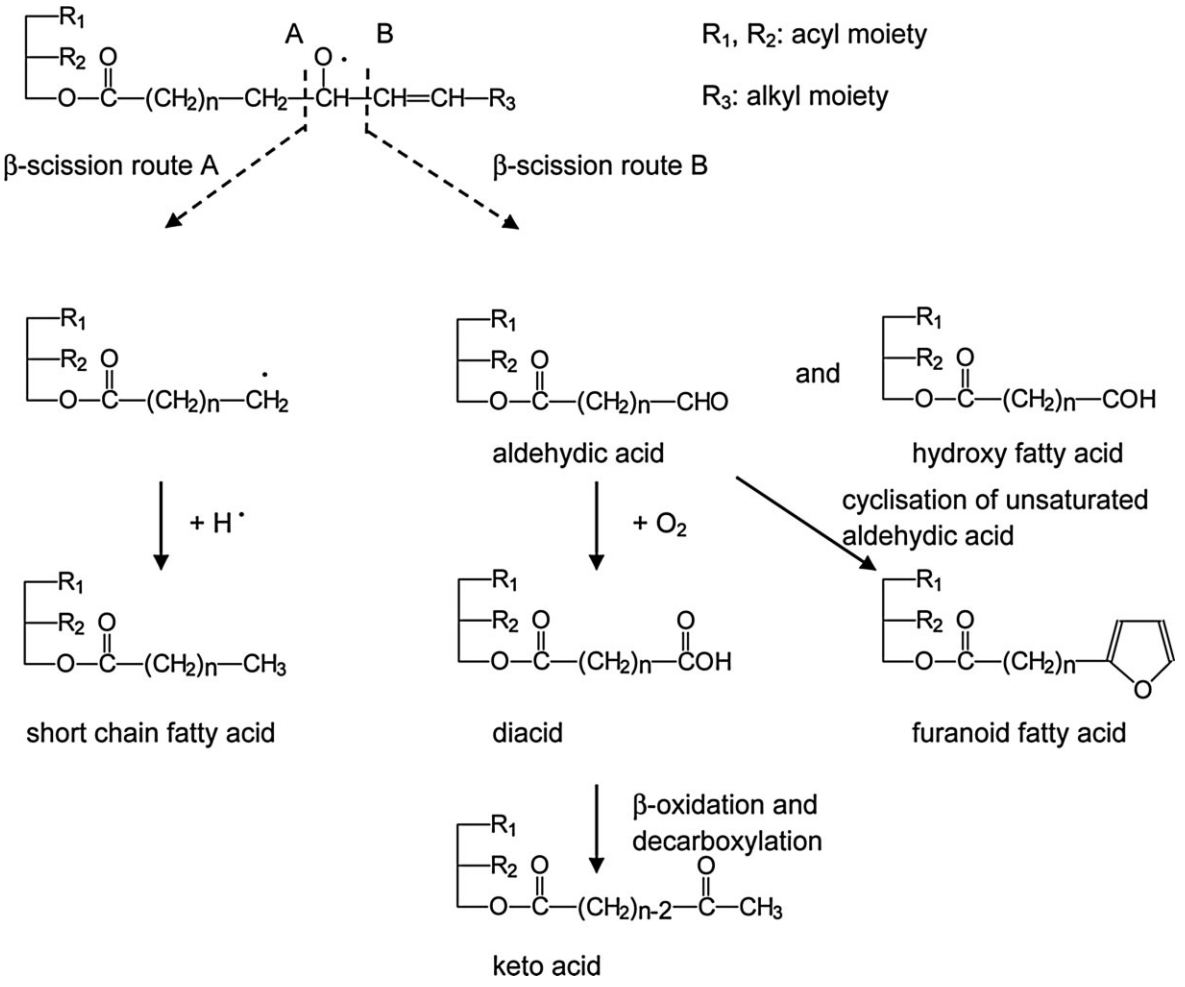

Figure 1. Formation of short chain degradation products during oxidation of triacylglycerides.

methods most often carried out in lipid laboratories. For methylation procedures base catalysed methods using potassium hydroxide or sodium methanolate in methanol resulted in best reproducibility and practically complete recovery [43]. Methyl nonanoate or methyl tridecanoate have proven to be absent at reasonable levels in all fats and oils and can be used as internal standard. GLC system performance should be checked to ensure an equal response for methyl nonanoate, -octanoate and -heptanoate [43, 44]. The determination of caprylic acid in the frying oil or in the fried goods will be compromised by small amounts of lauric or dairy fats due to their natural content of SCFA. These oils also comprise hexanoate and decanoate in similar amounts. So their presence is easily recognised in the chromatogram. In addition, heptanoate is not present at reasonable amounts in natural fats and oils and may serve as an uncompromised indicator for oxidation even in mixtures with lauric or dairy fats [42].

SCFA are formed to an extend of about 1–3 mg/g during reasonable frying conditions and due to their low content they are not of any health concern. However, the content of SCFA can be correlated to the contents of total polar matter (TPM) and polymeric TAGs (PTG), which are the most important parameters besides the sensorial properties to be met ensuring an acceptable frying oil quality during production [42–45]. At a level of 25 g/100 g TPM the frying oils reach a SCFA content of 0.9 to 1.8 mg/g according to the frying oil and heating temperature with a mean at 1.4 mg/g [44]. Other studies reported corresponding SCFA contents at about 1.7 mg/g at a TPM level of 25 g/100 g [42, 45]. As the correlation between SCFA and TPM is influenced by the heating temperature and other parameters this is only a limit for screening purposes and can not serve as a complementary legal limit like the limits for TPM and polymerised TAGs, which are the most common parameters for the quality assessment of frying fats and oils [42, 44].

1.5 Short chain aldehydic-, keto- and diacids

As described for the SCFA also short chain aldehydic acids can be formed, when the fatty acid radical interacts with a

hydroxy radical instead of a proton radical. They also remain esterified as aldehydic acid esters to the glycerol backbone of the TAGs. They can accumulate in the frying fat in the course of heating due to lack of volatility and may serve as a more reliable measure for oil degradation level assessments. The aldehydic compounds are covered under the term core aldehydes in order to differentiate them from the volatile aldehydes, which have received much attention for their relevance to the formation of the rancid off-flavour and in some cases for their toxicity. Aldehydic acids exhibit some reactivity and for instance di-acids can be formed during further oxidation reactions. Further oxidation of aldehydic acids will yield diacids like suberic acid and acelaic acid. In a subsequent step the formation of keto acids can be observed by decarboxylation of the monoesters of the diacids [46].

The analysis of aldehydic acids is often accomplished by a mild alkali catalysed transesterification with subsequent silica column fractionation in order to separate polar and unpolar substances. In a third step the fraction of polar substances was fractionated by HPSEC in order to separate short-chain oxidation products containing the aldehydic FAME from monomeric oxidised FAME and dimeric oxidised FAME. Finally, the aldehydic fatty acid methyl ester can be identified and determined by GC with mass spectrometric detection [46–48]. In addition a determination of the aldehydic acids as 2,4-dinitrophenylhydrazones was achieved using reversed phase HPLC and UV-detection [49].

Kamal-Eldin et al. detected up to 5 mg/kg of aldehydic fatty acids [47] with methyl 9-oxononanoate as the major compound followed by methyl 8-oxooctanoate, methyl 10-oxodec-8-enoate, methyl 11-oxo-9-undecenoate and methyl 12-oxo-9-dodecenoate in moderately used frying oils with a content of total polar compounds at 3–8 g/100 g. Here also mass spectra of the identified compounds and fragmentation patterns were presented and discussed.

Aldehydic fatty acids affect hepatic metabolism and especially enable hepatic lipid peroxidation [50, 51]. They are suspected to react in similar pathways as volatile aldehydes, are able to form aldimines with free amino groups and aldehydes with α,β-unsaturation and in addition they can react with sulfhydryl groups from proteins.

1.6 Long chain epoxy fatty acids

Oxidation of fatty acids by external hydroperoxides can lead to the formation of an epoxy ring at a double bond position. The epoxy ring can be oriented in *cis* and *trans* position with a prevalence for *trans* position. This is in contrast to enzymatically formed epoxy rings, which are substrate specific oriented and natural *cis* unsaturated fatty acids will lead to *cis* oriented epoxy rings, only. Therefor from oleic acid two isomers can be formed. Linoleic acid yields four isomers with epoxy rings at each double bond position and in addition also those isomers with one double bond and one epoxy ring, which give additional four possible isomers without differentiation of *cis* and *trans* double bonds. From linolenic acid there are 26 possible isomers. The fully epoxidised fatty acids are known from epoxydised soybean oil, which is a commercial plasticiser additive for poly vinyl chloride. This material is used for sealing lids from preserves [52].

Monoepoxy fatty acids were determined in thermoxidised olive, sunflower and used frying oils from restaurants and fried-food outlets by Berdeaux et al. and Velasco et al. [53, 54]. They found amounts of 3–14 mg/g oil in the samples from restaurants and in samples heated in a laboratory study. The monoepoxy fatty acids represent one of the major groups of oxidised altered fatty acid monomers beside polymers and dimers. They detected for similar levels of degradation a higher amount of monoepoxy fatty acids in the oil rich in oleic acid (olive oil) than in sunflower oil, which contains more linoleic acid. They attributed this effect to a lower tendency of olive oil to polymerisation and a greater thermal stability of the formed monoepoxy stearates compared to monoepoxy oleates, which are formed from linoleic acid and more susceptible to further reactions. In a survey from Switzerland even higher monoepoxy fatty acids contents were detected for frying oils in the range of 10–29 mg/g. However, the frying oils showed a content of polar material of 34–47 g/100 g exceeding the legal limits of most countries by far. In this survey also diepoxy fatty acids were covered by the analysis procedure but their content was negligible compared to monoepoxy fatty acids in the range of 0.005–0.02 mg/g oil [52].

The British Biological Research Association carried out a study on the toxicity of epoxidised soybean oil and determined a no adverse effect level at 140 mg/kg body weight and the lowest observed adverse effect was recognised at 1400 mg/kg body weight for rats fed a diet containing 5 g/100 g ESBO for 2 years [55]. From these data the Scientific Committee on Food in Europe specified a tolerable daily intake for epoxidised soybean oil at 1 mg/kg body weight. From the study there was no indication that ESBO is carcinogenic or genotoxic. Therefor one has to conclude that the concentration of epoxy fatty acids in used frying oils has to be considered as the major source of intake, because it exceeds by far the amount of epoxy fatty acids due to migration of ESBO into food from preserves.

1.7 Long chain keto-, hydroxy- fatty acids

These fatty acid degradation products can be formed from the hydroperoxide precursors as shown as an example in Fig. 2. However, compared to epoxy fatty acids there are only few data available for these substances. Their determination by GC is complicated by overlapping peaks. For the keto fatty acids the position of the keto group was tentatively assigned as 9- and 10-keto stearate [56] or as 9- and 13-ketostearate [57]. In the later reference hydrogenation was carried out in order to simplify the peak identification and to improve the peak separation. As hydroxyl fatty acids 9- and 10-hydroxy-octadecanoate, 9- and 10-hydroxy-octadec-12-enoate and

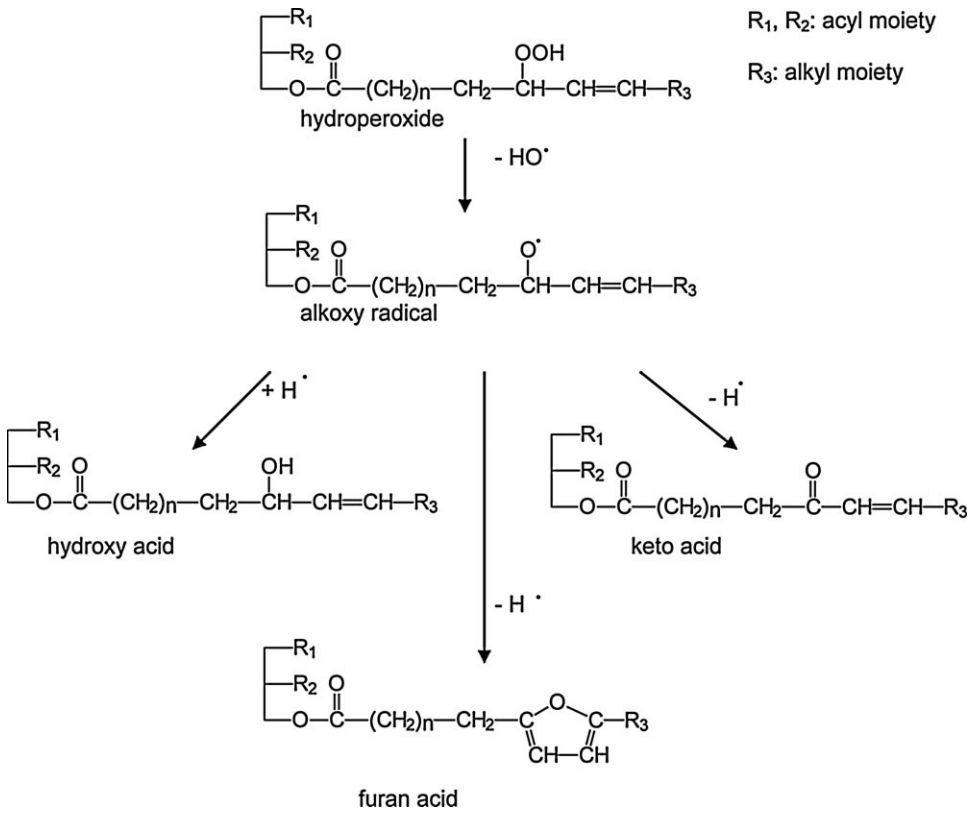

Figure 2. Formation of long chain degradation products during oxidation of triacylglycerides.

12- and 13-hydroxy-octadec-9-enoate were identified [58]. Keto- and hydroxy fatty are found in similar amounts along with the epoxy fatty acids. Keto acids were determined in French fries at a level between 1.2 and 10.2 mg/kg in different oils used for frying for up to 8 h compared to 4.9–186 mg/kg of the sum of epoxy- and keto fatty acids [56]. This corresponds to a content of 7.1–55 mg/kg for keto acids and a level of 257–993 mg/kg for the sum of epoxy- and keto fatty acids in the oil of the par fried and in the oil finally absorbed by French fries, respectively. In another study the level of epoxy-, keto- and hydroxy fatty acids were determined in sunflower oils after thermoxidation for 10 h at 180°C at 1.3–4.4 g/kg for epoxy fatty acids, 0.5–2.5 g/kg for keto fatty acids and 1.9–5.5 g/kg for hydroxy fatty acids [57]. The studies are not necessarily contradictive and give a first indication about the quantitative levels of keto- and hydroxy fatty acids, for oxidation rate is higher during thermoxidation compared to real frying operation with the protective effect of repeated water blanket.

For hydroxy fatty acids as in castor bean oil with a high content of about 85 g/100 g ricinoleic acid a laxative effect is known. However, the amount of hydroxyl fatty acids found in frying oils and fried foods is very low compared to castor bean oil and the effect of polymerised triglycerides seems to be more important in this respect.

1.8 Furan fatty acids

Oxidative degradation of unsaturated fatty acids may lead to the formation of furan fatty acids, which contain a furan ring in the fatty acid chain [46, 59]. The *trans*,*trans*-isomers of CLA are reported to be most susceptible to further oxidation and showed highest yields for furan fatty acids [59]. In spite that furan fatty acids have been identified in heated TAGs [46] there is no data published for their contents in frying fats, yet.

However, there are also natural sources for furan fatty acids as from fish liver at 4000 mg/100 g and fish fillet at 900 mg/100 g down to plant oils at 5–42 mg/100 g [60]. In addition furan fatty acids are known to be present in cholesterol esters and TAGs of ruminant liver [61] and in human phospholipids like phosphatidyl ethanolamine and -choline [62]. Furan fatty acids from fresh fish contain a methyl group at the ring carbons, while furan fatty acids from oxidative degradation do not contain these groups. This difference might influence their safety evaluation [63], because their enzymatic oxidation products show different stabilities. Naturally occurring methyl substituted furan fatty acids yield very unstable dioxoenes, while those from oxidation products are more stable [64]. It has been observed that furan fatty acids with alkyl moieties at the ring act as

antioxidants, while furan fatty acids from oxidation do not show any antioxidant effects [65].

1.9 Di- and polymerised fatty acids

Di- and polymerisation of fats and oils proceeds during frying and therefor in many countries limits for polymerised TAGs have been set up at about 12 g/100 g. Polymers compose of oxidised and non-oxidised fatty acids, which can be differentiated by a combination of the isolation of polar compounds and SEC after a mild transesterification to FAME [66]. Used frying oils from restaurants and fried food outlets with polar compounds in the range of 33–53 g/100 g contained 13.6–38.4 g/100 g of polymerised and dimeric TAGs. In order to focus on di- and polymerised fatty acids instead of di- and polymerised triaclyglycerols in these frying oils the samples were additionally analysed. In a first step they were transesterified and then the polar and the non-polar fraction of the FAME were isolated by column chromatography on silica gel. In both, the polar and the non-polar fractions the di- and polymerised fatty acids were determined by HPSEC. The sum of the non-polar fatty acid dimers, oxidised fatty acid dimers and fatty acid polymers increased during frying and reached a level of 11.0–22.8 g/100 g [66].

Dimeric and polymeric triglycerides and also dimeric fatty acids in used frying fats show low resorption rates in contrast to other degradation products deriving from oxidation like oxidised monomeric and dimeric acids, oxidised cyclic fatty acids and other polar compounds [67]. The fraction of polymerised material from oils severely overheated at 250°C to 300°C for to 24 h protected from oxygen in sealed vials caused diarrhoea fed at 20% in the diet to rats [68]. Other studies pointed out that dimeric fatty acids and triglycerides show low toxicity during rat feeding [69–71]. The intact non-polar dimeric fatty acids together with the monomeric oxidised fatty acids have been analysed directly by high temperature GLC in the polar fraction of the total polar material after preparation of the methyl esters by alkaline catalysed reaction [72]. The results were in good correlation to those obtained by HPSEC.

2 Conclusion

The different alterations due to heat and oxygen exposure during frying yield in isomerisation, oxidation and polymerisation products. Also combinations of several mechanisms can be observed. Polymerised products show only weak physiological effects due to their limited absorption. Heat induced isomerisation during frying increases the content of TFA to a low extend only, which is not significant for physiological effects. The toxicological relevance of cyclic fatty acids has not been finally assessed, but may be of minor relevance due to the low quantity. Therefore most attention and further work should be focused on the oxidised monomeric TAGs containing epoxy, aldehydic and keto fatty acids.

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