

Influence of Heating Time and Metal Ions on the Amount of Free Fatty Acids and Formation Rates of Selected Carbonyl Compounds during the Thermal Oxidation of Canola Oil

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Canola oil was heated continuously for 8 h at a typical frying temperature (180 °C) in the presence of various concentrations of the metal ions Fe(III), Cu(II), and Al(III) (9.2, 27.5, and 46.0 $\mu\text{g L}^{-1}$ of oil) to evaluate changes occurring in the amount of free fatty acids, expressed as acidity index, and in the formation rates of aldehydes. The aldehydes were collected and derivatized in silica cartridges functionalized with C18 and impregnated with an acid solution of 2,4-dinitrophenylhydrazine, after which they were eluted with acetonitrile and analyzed by LC-DAD-MS. Among the substances emitted, the following were identified and quantified: formaldehyde, acetaldehyde, acrolein, propanal, butanal, hexanal, (*E*)-2-heptenal, and octanal. During heating of the oil, the compounds presenting the highest mean formation rates were acrolein, hexanal, and acetaldehyde. In the study of the metal ions, the addition of ions to the samples generally led to a corresponding increase in the formation rates of the eight substances. The compounds showing the highest relative increases in formation rates were formaldehyde, acetaldehyde, propanal, and heptenal. In terms of catalytic effect, copper proved to be the most efficient in promoting increased formation rates, followed by iron and aluminum.

KEYWORDS: Canola oil; thermal oxidation; aldehydes; formation rates; metal ions; LC-DAD-MS

INTRODUCTION

Frying is a very common form of cooking in the cuisine of several countries because it is a rapid process that results in products with pleasant organoleptic characteristics such as flavor, aroma, and texture.

During the process of frying food, vegetable oils are exposed to high temperatures in the presence of atmospheric oxygen, which alters their physical and chemical characteristics (1, 2). These changes produce visible modifications such as darkening of the oil, increased viscosity, and formation of foam and smoke, which are also responsible for the development of unpleasant flavors and odors. They also cause other alterations that affect the food's nutritional quality due to the degradation of liposoluble vitamins and essential fatty acids, besides affecting food integrity and safety by forming compounds that are potentially toxic to human health (3).

The main degradation route of oils and fats is thermal oxidation, a spontaneous phenomenon that leads to chemical changes during the processing, storage, distribution, and consumption of oils (4). The main products of oxidation include hydrogen peroxides and secondary products of oxidation such as aldehydes, ketones, alcohols, fatty acids, cyclic monomers, and products of polymerization (1, 5, 6). Among them, aldehydes stand out as the products formed in greater abundance than other possible products (7).

The intensity of these reactions depends on several factors such as the type of oil employed, heating time and temperature, type of

food, surface-to-volume ratio, materials used to cook the food, and the presence of antioxidants and metal ions (6, 8).

There are several kinds of cooking oils on the market, each with its own profile regarding fatty acid and glyceride contents. Some studies have reported that formation of volatile aldehydes depends on the composition of the cooking oil (9); oils with high contents of polyunsaturated fatty acids are more prone to oxidation than those with low contents (10).

Trace levels of metal ions in oils are considered to be responsible for increasing lipid oxidation, which reduces their nutritional quality and leads to the formation of undesirable compounds such as formaldehyde and acrolein (11, 12). Metals such as iron, copper, and aluminum are usually found in trace concentrations in vegetable oils, as well as in the composition of certain foods and domestic utensils (11–13). Metal ions act as catalysts for lipid oxidation through the homolytic cleavage of hydrogen peroxides and/or by direct attack on lipids, generating fatty acid radicals (14).

The changes that take place in edible oil during processing, storage, and especially heating in the presence of oxygen are extremely important, not only from an economic standpoint, through losses resulting from reduced shelf life, but also due to the possible formation of compounds potentially toxic to health. Studies with vegetable oils have discovered, in their vapor fraction, the presence of compounds harmful to health, such as acetaldehyde and acrolein (10, 15).

Acetaldehyde may be cancerous for humans and has shown toxic properties in several studies (16, 17). Acrolein vapors may lead to serious respiratory problems and eye irritation (18). It has

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also been reported to cause decreased heart rate and elevated blood pressure in rabbits (16), as well as to inhibit the p53 tumor suppressor protein, thus possibly contributing to the formation of lung cancer (19).

Acrolein is commonly present in both indoor and outdoor air. The indoor sources of acrolein may be several, all of them related to human activities, including heated cooking oil (1, 10, 15, 20, 21). Seaman et al. determined an indoor half-life for acrolein of 14.4 h, showing that vapor concentrations generated during cooking events may remain within the cooking places for many hours, particularly when the air exchange rates are low (21).

The aim of this work was thus to determine the formation rates of aldehydes by canola oil, heated continuously to 180 °C for 8 h, with and without the addition of Fe³⁺, Cu²⁺, and Al³⁺ ions at different concentrations (9.2, 27.5, and 46.0 μg L⁻¹). The choice of canola oil was based both on its widespread use in the culinary habits, because it is considered one of the most healthful edible oils, and on its high content of omega 3 and monounsaturated fatty acids. A typical average fatty acid composition of canola oil is given as follows: 18:0, 18%; 18:1, 63%; 18:2, 20%; and 18:3, 8.3% (10). The free fatty acid compositions were also determined in each case, for a better characterization of the oil degradation.

To carry out these studies, the vapors emitted by the oil were collected in silica cartridges functionalized with C18 and impregnated with an acid solution of 2,4-dinitrophenylhydrazine and were then analyzed by liquid chromatography (15). The carbonyl compounds (CC) identified in the vapor emissions were formaldehyde, acetaldehyde, acrolein, propanal, butanal, hexanal, (*E*)-2-heptenal, and octanal.

MATERIALS AND METHODS

Chemicals and Standards. All of the chemicals employed in this study were of either analytical or spectroscopic/chromatographic grade. 2,4-Dinitrophenylhydrazine (DNPHi) and 2,4-dinitrophenylhydrazone (DNPHo) standards of the carbonyl compounds acetaldehyde, acrolein, propanal, butanal, hexanal, (*E*)-2-heptenal, and octanal were purchased from Merck (Darmstadt, Germany) and Sigma-Aldrich (Milwaukee, WI). FeCl₃, AlCl₃, and CuCl₂ solutions (9.2 mg L⁻¹ in metal) were prepared by weighing the solids in volumetric flasks and dissolving them with ethanol (FeCl₃ and CuCl₂) or a 4:1 ethanol/water mixture (AlCl₃). Deionized organic-free water was prepared in a Barnstead NANOpure Diamond system.

DNPHo Standard Solutions. From a stock solution, work standards were prepared in the range of 0.1–1.4 μg mL⁻¹ by transferring the DNPHo of each carbonyl compound to a volumetric flask and dissolving it in 10 mL of acetonitrile. All of the standard solutions were stored under refrigeration at 4 °C in amber glass bottles.

Preparation of Sampling Cartridges. The cartridges (Sep-Pak Classic C₁₈, 360 mg, Waters, Milford, MA) were impregnated with 4 mL of a 0.8% w/v DNPHi acid solution (60% CH₃CN/39% H₂O/1% H₃PO₄) and then dried in a gentle stream of UP grade nitrogen for 5 min (22). After this, they were sealed with Teflon tape, wrapped in aluminum foil, and placed in hermetically closed plastic bags, which were stored under refrigeration until sampling. DNPHi impregnated cellulose filters were placed inside the plastic bags to trap any CC that might be present as contaminant in the air (23).

Samples. To minimize the natural heterogeneity between different commercial brands of oil, a mixture (1 L) was prepared using four different brands purchased in local markets of Salvador, Bahia. The bottles were selected from the backs of the shelves, where they were protected from light. The prepared samples were poured into amber glass bottles, under a nitrogen flow, and stored away from light. Whenever aliquots of a sample were collected, the bottles were purged with a nitrogen flow before capping to prevent oxygen traces during storage.

Experimental Setup. The experimental setup was mounted according to a previous work (15). Briefly, 200 mL of the oil sample was put into a 500 mL round-bottom glass flask and, while heating under continuous stirring, a flow (1 L min⁻¹) of purified air was passed through it. During the experiments, oil samples were heated continuously to 180 °C for 8 h.

The experiments were carried out in triplicate, and the surface-to-volume ratio used was 0.43 cm⁻¹. The carbonyl compounds emitted by the oil samples during the experiments were collected, each hour, using two Sep-Pak cartridges connected in series, for 5 min at a 0.2 L min⁻¹ sampling flow rate. After sampling, the hydrazones were eluted with acetonitrile directly into an amber vial, and the final volume was topped off to 5 mL before analysis.

Addition of Metal Ions. To determine the influence of Fe(III), Cu(II), and Al(III) ions on the CC formation rates, these metal ions were added independently to the oil samples before heating, at concentrations of 9.2, 27.5, and 46.0 μg L⁻¹, which, on a weight/weight basis, were equivalent to concentrations of, respectively, 10, 30, and 50 μg kg⁻¹ of oil. The experiments were then carried out in triplicate, in the same way as described above.

HPLC Analysis. The carbonyl hydrazones were separated in an X-Terra MS C₁₈ column (2.1 × 250 mm, 5 μm, Waters) and analyzed in an Agilent 1100 LC-DAD-MS system (Agilent, Waldbronn, Germany) Bruker Esquire 3000 plus (Bruker, Billerica, MA) according to the following conditions: flow rate, 0.25 mL min⁻¹; gradient of water (A) and acetonitrile (B), from 40 to 100% B in 30 min, then 100% B for 6 min, returning to 40% B in 4 min, and remaining for 5 min, making a total run time of 45 min. Quantification of the aldehydes, as the respective hydrazones, was done by external calibration curves, and the absorbance of compounds was monitored at 365 nm. The analytical curves were built with seven points, each one injected in triplicate. Concentration of the standards ranged from 0.1 to 1.4 μg mL⁻¹. New curves were built every 15 days, but they were daily checked by analysis of an intermediary standard. The correlation coefficients (*r*) were > 0.999 for all of the curves. To identify the carbonyl hydrazones present in samples, by association with their retention times in the DAD chromatograms, one standard mixture and two oil samples from different experiments were also analyzed in the mass spectrometer. The MS conditions were as follows: source, ESI in negative ionization mode; nebulizer pressure, 22.0 psi; dry gas flow, 10.0 L min⁻¹; dry gas temperature, 300 °C; capillary voltage, 4000 V.

Free Fatty Acid Content. The free fatty acid content of the samples was determined according to AOCS method Ca 5a-40 (24). Samples were analyzed before heating (0 h) and after 1 and 8 h of continuous heating.

RESULTS AND DISCUSSION

Free Fatty Acid Content. Figures 1, 2, and 3 show the free fatty acid content (AI) as a function of heating time, with and without the addition of Al(III), Fe(III), and Cu(II) ions, respectively, at different concentrations. As can be seen, the indices increased with heating time both with and without the addition of metal ions. Before heating, there were no significant differences among the AI values of samples without added metals and with Al(III) or Cu(II) ions. For samples with Fe(III), on the other hand, a slight increase was observed in the AI, especially when this ion was present at its highest concentration.

As samples were heated, the AI increments were higher in the presence of the metal ions, and the higher their concentrations, the higher the increments observed. This effect was more pronounced when samples were heated in the presence of Cu(II) and Fe(III), even after only 1 h of heating. In absolute values, the highest AI increments occurred in samples heated for 8 h in the presence of Cu(II) (67% of increment), Fe(III) (51% of increment), and Al(III) (29% of increment) at a concentration of 46.0 μg L⁻¹.

If the free fatty acid content were considered to be the only quality criterion for the acceptableness of the oil studied in this work, the presence of these metal ions at the concentrations evaluated would not render it unacceptable, because the AI values found were always below those considered to be the limit to discard the product according to the Brazilian Association for Consumer Protection (25), which is 0.9% of oleic acid, and also according to American legislation, which is 1% (26). However, the free fatty acid content cannot be used as the single evaluation parameter but must be associated with other quality indicators, because free

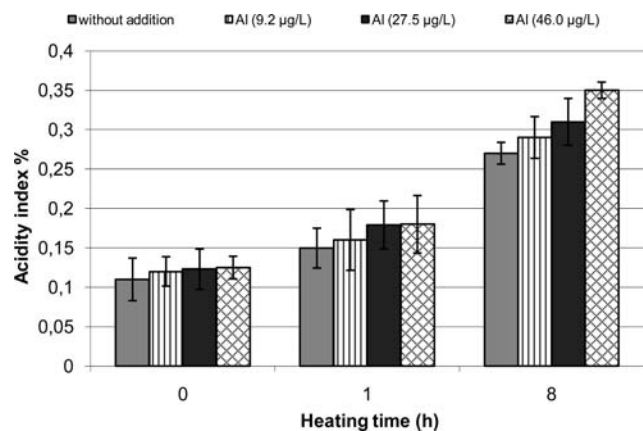


Figure 1. Free fatty acid content as a function of heating time, with and without the addition of Al^{3+} , at different concentrations.

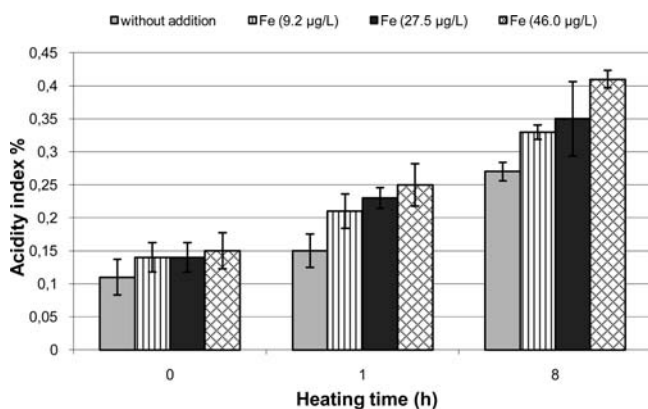


Figure 2. Free fatty acid content as a function of heating time, with and without the addition of Fe^{2+} , at different concentrations.

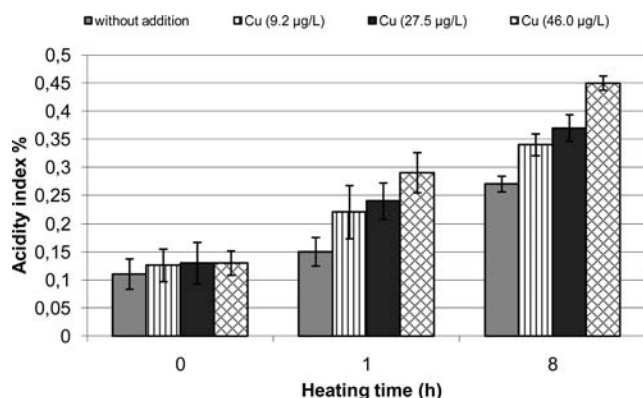


Figure 3. Free fatty acid content as a function of heating time, with and without the addition of Cu^{2+} , at different concentrations.

fatty acids may undergo oxidation processes, generating secondary products that are also deleterious to the oil's quality (27).

Formation Rates of Aldehydes. The CC formed along the heating of the oil samples were confirmed in two samples analyzed by LC-ESI-MS in the negative mode, through the $[\text{M} - \text{H}]^-$ ion of their respective hydrazones. To give an example of the spectra obtained, **Figure 4** shows the mass spectra of the hydrazones of acrolein and hexanal.

Figure 5 shows the formation rates of aldehydes by canola oil heated continuously at 180 °C for 8 h. The values represent the average of eight measurements; these experiments did not involve the addition of metal ions.

Among the aldehydes quantified, acrolein presented the highest formation rates, followed by hexanal and acetaldehyde. The mean values of formation rates ranged from 79.0 ± 1.3 to $1662.1 \pm 21.3 \mu\text{g h}^{-1} \text{L}^{-1}$ for formaldehyde and acrolein, respectively.

Acrolein (2-propenal) is a monounsaturated aldehyde, the toxicity of which is due to its reactivity with sulfhydryl groups in proteins and glutathione, leading to interferences in the intermediary cell metabolism and modifying proteins by introducing inter- and intramolecular cross-linkages (28–30). It has been associated with several illnesses, such as atherosclerosis, Alzheimer's, and even cancer (7, 29, 31). If $75 \mu\text{g m}^{-3}$ is considered to be the concentration level of acrolein in the air at which most people will experience irritation and/or discomfort during periods as short as 10 min (21), and due to its reported indoor half-life of 14.4 h (21), it could be possible, in some cases, that people in cooking places would be exposed to that level, or even higher. With regard to the EPA inhalation reference concentration ($0.002 \mu\text{g m}^{-3}$) and chronic exposure limit ($0.5 \mu\text{g kg}^{-1} \text{day}^{-1}$) (32), the first would be certainly exceeded, whereas the second probably would be in some cases.

The profile of the formation rates was similar to that reported in our previous work on palm oil (15), although different absolute values were observed in each case. This suggests that the fatty acid composition in these oils did not affect significantly the relative order in which the aldehydes were formed and then emitted.

In another work (7) it was found that hexanal was the dominant alkanal produced from high-oleic safflower oil during heating at 180 °C under low-oxygen atmospheres.

When these results are compared with those of three other studies with heated (180 °C) canola oil, when the formation rates of alkanals and alkenals are considered, in one of them (10) there was agreement, with acrolein and hexanal as the most emitted. In the second study (33), nonanal and 2-heptenal were reported as the most emitted, whereas acrolein was only the sixth most emitted; on the other hand, hexanal and formaldehyde were not determined and acetaldehyde was not detected. This work also stated that, among the oils studied (coconut, safflower, canola, and extra virgin olive), canola oil generated the lowest amount of potentially toxic volatile aldehydes.

Finally, the third paper (1) reported nonanal and 2-decenal as the most emitted, whereas acrolein was not identified as present in vapor emissions. According to the authors, the experimental conditions applied in this study were not able to trap low molecular weight CC, such as acetaldehyde and acrolein, among others. In the present work nonanal was not determined because its standard was not available.

Different studies have suggested a correlation between the type of volatile aldehyde emitted and the fatty acid composition of the cooking oil (9, 10). The highest formation rates of acrolein by canola oil can be explained, in part, by the small amounts of linolenic acid in the composition of this oil (~5.6%). The formation of acrolein can follow different pathways, such as thermolysis of glycerol from acylglycerol hydrolysis (7, 15, 20). Because these experiments did not involve the addition of foods and therefore no water was added to the system, other pathways were likely the main factors responsible for its formation (10). According to a mechanism proposed by Da Silva and Pereira (15), a possible pathway is the oxidation of linolenic acid.

With regard to hexanal, the second most emitted aldehyde in the experiments, the main pathway for its formation was probably the oxidation of linoleic acid, which begins with a hydrogen abstraction in the C11 and is followed by an oxygen addition in the C13, as illustrated in **Figure 6**. The hydrogen abstraction from the C11 is easier, because the radical formed will be part of an allylic system in the molecule's structure and thus stabilized by resonance.

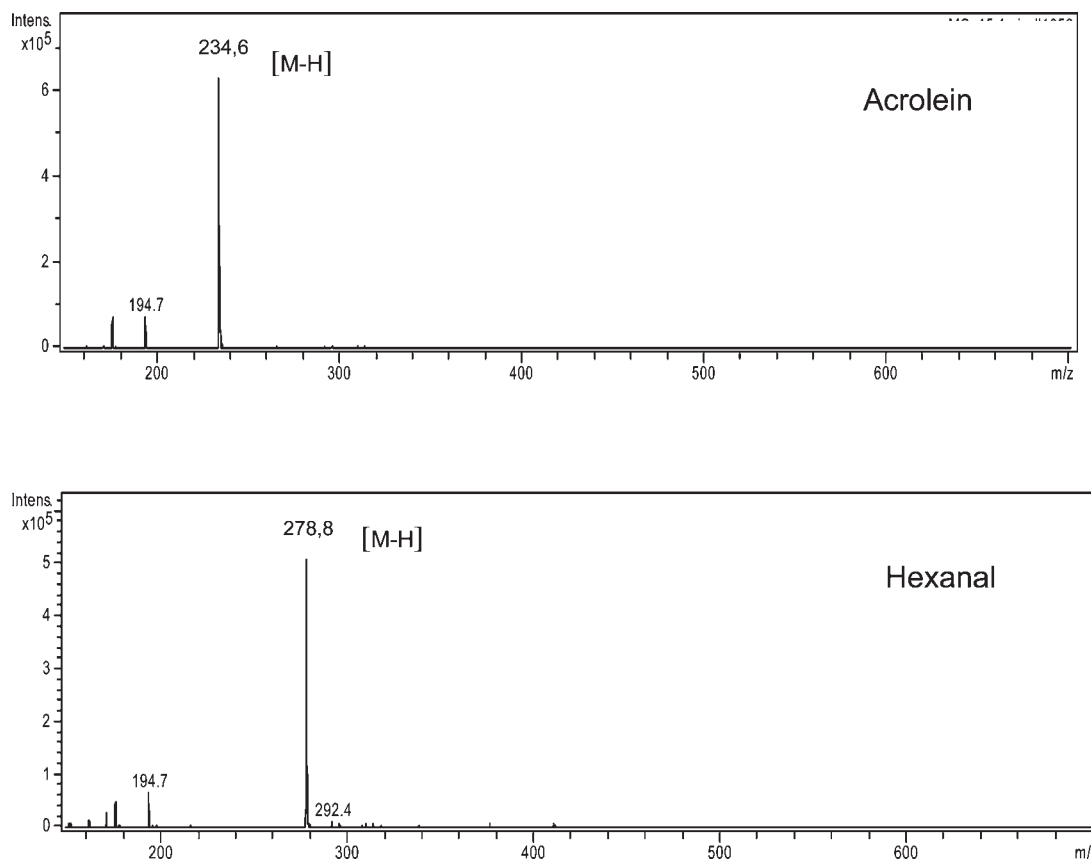


Figure 4. Mass spectra of the hydrazones of acrolein (A) and hexanal (B), obtained by ESI in the negative mode, of oil samples heated for 1 h.

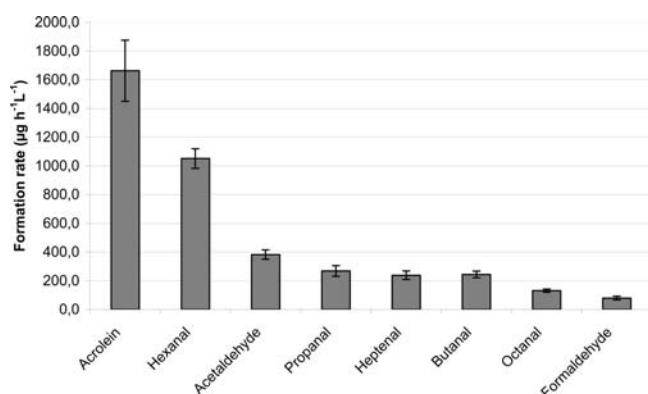


Figure 5. Mean formation rates of aldehydes by canola oil when continuously heated at 180 °C through 8 h.

Mean Formation Rates of Aldehydes in the Presence of Metal Ions. Figures 7 and 8 show the mean formation rates of identified CCs by canola oil heated at 180 °C for 8 h in the presence of the three metal ions at different concentrations.

In general, the formation rates increased when metal ions were added to the oil samples, even at the lowest concentration level evaluated ($9.2 \mu\text{g L}^{-1}$), as in the case of formaldehyde, acetaldehyde, acrolein, propanal, and hexanal. On the other hand, the increase in butanal, heptenal, and octanal formations was only relevant at metal ion concentrations of 27.5 or $46.0 \mu\text{g L}^{-1}$. These results are consistent with those obtained for the acidity indices, which showed an increase in the average values of this parameter in response to the addition of metal ions to the oil samples, and also with those of other authors who show an increase in the oil oxidation with the addition of metals (13, 34).

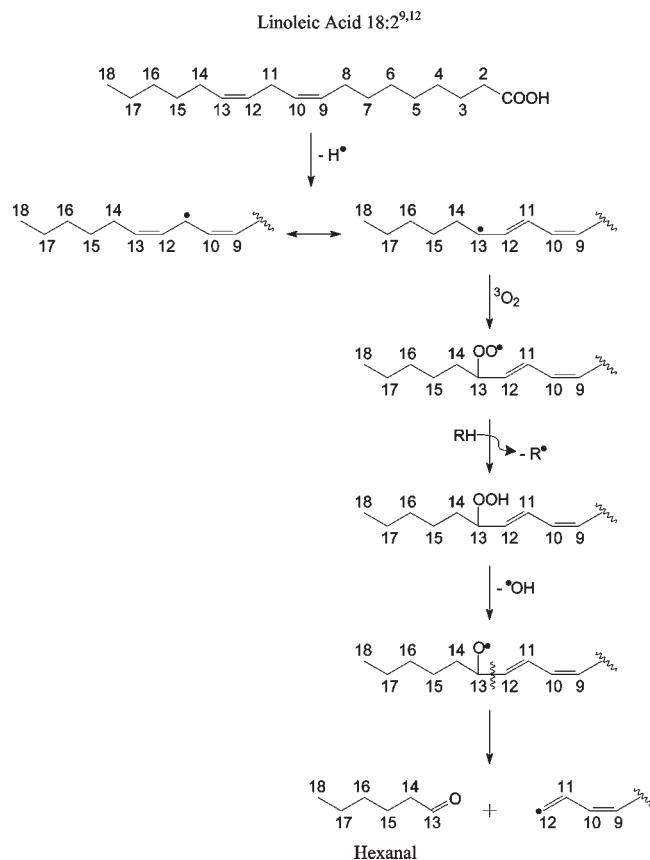


Figure 6. Formation scheme for hexanal from the oxidation of linoleic acid.

With regard to the eight identified CCs, formaldehyde, acetaldehyde, propanal, hexanal, and heptenal showed the highest

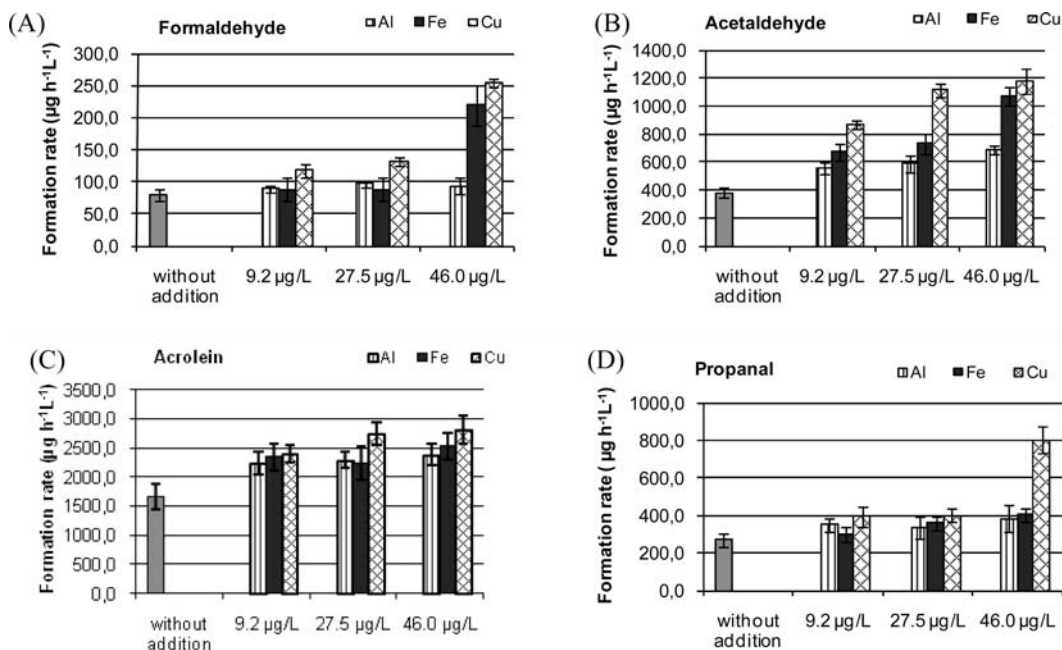


Figure 7. Mean formation rates of formaldehyde (A), acetaldehyde (B), acrolein (C), and propanal (D) by canola oil, when continuously heated at 180 °C through 8 h and in the presence of the studied metal ions at different concentrations.

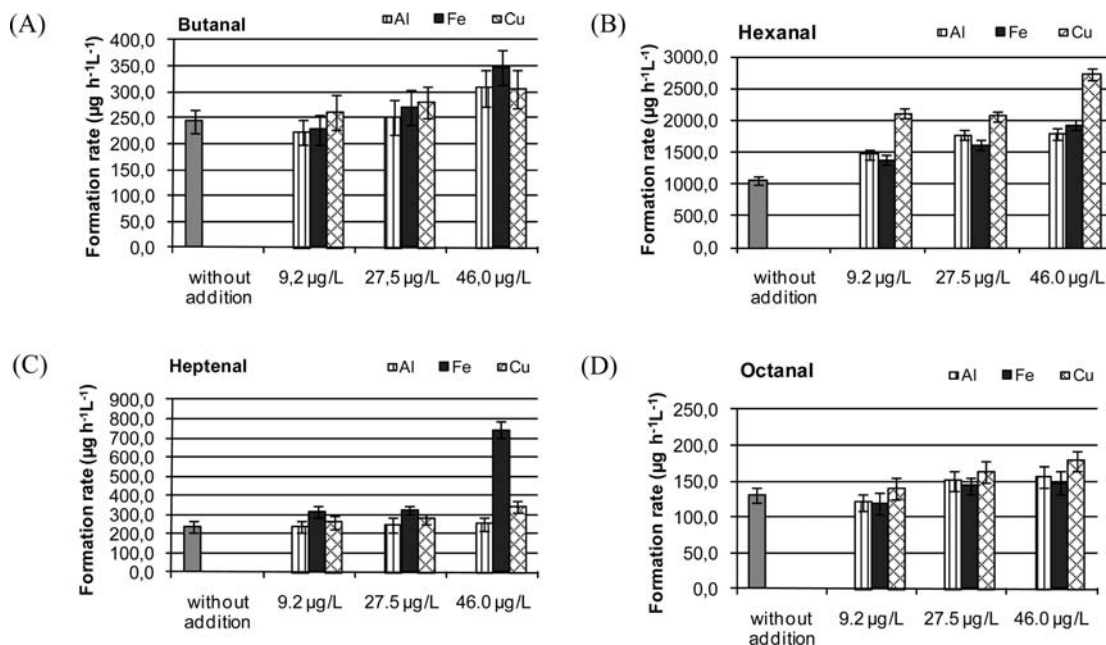


Figure 8. Mean formation rates of butanal (A), hexanal (B), heptenal (C), and octanal (D) by canola oil, when continuously heated at 180 °C through 8 h and in the presence of the studied metal ions at different concentrations.

relative increases in their formation rates, with variations of about 3-fold compared with the samples without added metal ions. The highest increases were generally observed in the presence of Cu^{2+} or Fe^{3+} at their highest concentration level (46.0 $\mu\text{g L}^{-1}$).

The CC showing the highest formation rate in this study was acrolein, which increased about 2-fold in response to the addition of Cu^{2+} ions at concentrations of 27.5 or 46.0 $\mu\text{g L}^{-1}$.

Among the three metal ions evaluated, Cu^{2+} generally showed the strongest catalytic effect on CC formation rates, followed by Fe^{3+} and Al^{3+} . Copper and iron, as transition metals, are prone to form complexes and thus to stabilize intermediary species such as those possibly formed during the thermal oxidation of oils. Moreover, they are able to react with hydrogen peroxides, according to reactions 1 and 2, giving rise to alkoxide and peroxy radicals that may propagate

the oxidation processes (34). Recently, the generation of singlet oxygen in the reaction of lipid hydroperoxides with biologically important oxidants, such as metal ions, was demonstrated (35). The peroxy radical may react with other lipids, promoting both the propagation of the peroxidation process and reactions with other radicals present in the oil, giving rise to secondary species of greater reactivity and toxicity, such as aldehydes and ketones (35).



The ability of the metal ion to promote these reactions is due to the relatively easy change of its oxidation number between the $\text{M}^{(n+1)+}$

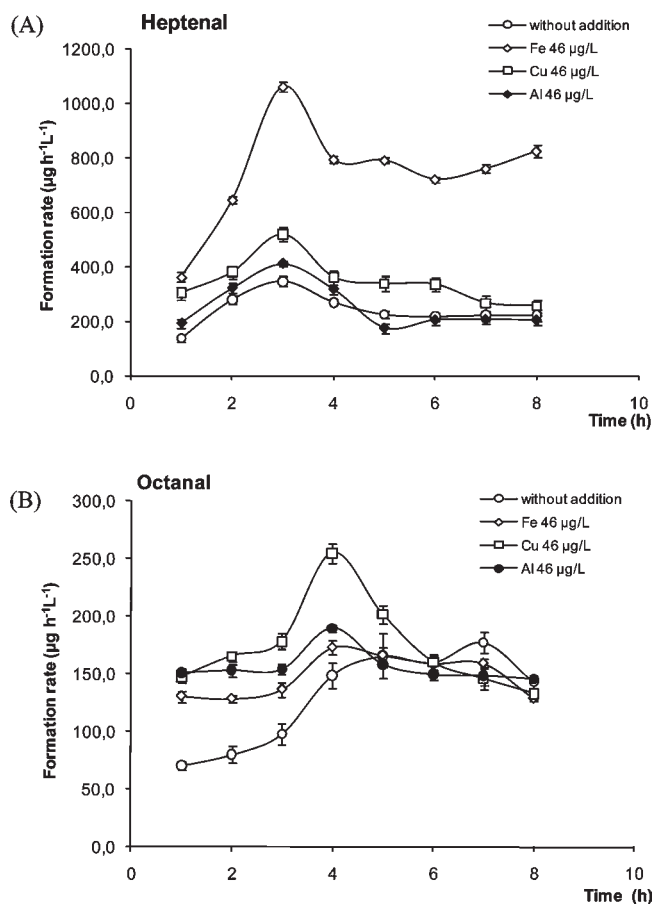


Figure 9. Formation profiles of octanal and heptenal, when continuously heated at 180 °C through 8 h and in the presence of the studied metal ions at 46 µg L⁻¹ concentration.

and Mⁿ⁺ states in the reaction media during the process. The lower the potential value, the easier this change. Considering the low Cu²⁺/Cu⁺ redox potential in water ($E^\circ = +0.161$ V) (36) and assuming this tendency persists in the oil matrix, the best catalyst among the metal ions evaluated in the oxidation reactions and in the formation of the identified CC would be copper, as was observed.

With respect to the formation profiles of aldehydes during the 8 h of heating, with and without added metal ions, some of them showed no changes but only increased formation rates. Other aldehydes, however, showed shifts in their maxima as a function of the metal ion species added to the sample. **Figure 9** shows the formation profiles of octanal and heptenal as a function of heating time. These aldehydes illustrate the two aforementioned situations. Our results suggest that the species of metal ions added may influence not only the average formation rates but also the time required for some aldehydes to reach their maximum formation rates.

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