

## Influence of Time, Surface-to-Volume Ratio, and Heating Process (Continuous or Intermittent) on the Emission Rates of Selected Carbonyl Compounds during Thermal Oxidation of Palm and Soybean Oils

THALITA OLIVEIRA DA SILVA<sup>#</sup> AND PEDRO AFONSO DE PAULA PEREIRA\*

Instituto de Quimica, Universidade Federal da Bahia, Campus Universitário de Ondina,  
 40.170-290 Salvador, BA, Brazil

The aim of this work was to compare the emission rates of selected carbonyl compounds (CC) produced by palm and soybean oils when heated at 180 °C in the presence of air, through different time intervals and at different surface-to-volume ratios (*S/V*), in continuous and intermittent processes. The CC were collected and derivatized onto silica C18 cartridges impregnated with an acid 2,4-dinitrophenylhydrazine solution, followed by extraction with acetonitrile and analysis by HPLC-UV and, in some cases, HPLC-MS with electrospray ionization. Among the CC quantified, namely, acetaldehyde, acrolein, propanal, butanal, hexanal, 2-heptenal, and 2-octenal, acrolein was the main emission in both oils and all *S/V* ratios, followed by hexanal and 2-heptenal. The soybean oil has presented greater emission rates of acrolein than palm oil. When different *S/V* ratios used during the heating process of the oil were compared, the emission rates, in general, were directly related to them, although saturated and nonsaturated CC have had different behaviors toward oxidation reactions. During intermittent heating, there was a trend of increasing emission rates of saturated aldehydes, whereas the opposite was observed with unsaturated aldehydes, probably due to the reactivity of the double bond present in these compounds.

**KEYWORDS:** Palm and soybean oils; thermal oxidation; aldehyde emissions; HPLC; DAD; ESI-MS

### INTRODUCTION

In the food-frying process, vegetable oils need to be continually or intermittently exposed to high temperatures in the presence of atmospheric oxygen, which promotes changes of their physical and chemical characteristics (1). The heating process of oils results in damages, which can generate several types of compounds (2), through reactions such as oxidation and polymerization of the acylglycerols (3), which are the basic constituents of the oil.

The thermal oxidation products include hydroperoxides and secondary oxidation products such as volatile and nonvolatile carbonyl compounds (CC; aldehydes, ketones), cyclic fatty acid monomers, and polymerization products (4). Among these, aldehydes seem to be the most important because they are the most abundant when compared to the other possible products (5).

Some of these volatile aldehydes can be harmful to humans, for example, acetaldehyde and acrolein. Acetaldehyde is possibly carcinogenic to humans and has shown toxic properties in several studies (6, 7). Acrolein vapors can lead to acute respiratory and ocular irritations (8) and is reported as causing

heartbeat reduction and blood pressure elevation in rabbits (5, 9). As these CC can be emitted to the air during the heating process, they may induce undesirable effects, for example, to cooks (5, 10).

The intensity at which degradation reactions occur depends on several factors, such as the temperature and duration of heating, the oil's surface to volume ratio, and the heating process, either continuous or intermittent, as well as the atmospheric oxygen concentration above the oil's surface (2, 5, 11, 12). The type of oil used is also an important factor to be taken into account in the study of degradation. Vegetable oils that contain large amounts of polyunsaturated fatty acids (PUFA) in their composition are more prone to oxidation than are oils with a larger content of saturated fatty acids (SFA) (11). Moreover, the oil's initial conditions resulting from its manufacturing processes (the temperature employed, addition of synthetic antioxidants, antifoaming agents, etc.), as well as the presence of trace levels of elements such as metals and the presence of natural antioxidants, are important factors for its stability (13).

Studies involving olive and rapeseed oil heated to 180 and 240 °C (14) have revealed the formation of seven alkenals, eight 2-alkenals, and 2,4-heptadienal, the formation rates of which proved to be dependent on the heating temperature. In another study involving seven different types of fats and oils heated to 190 and 240 °C for 8 h/day up to a critical state in terms of

\* Corresponding author (e-mail pedroapp@ufba.br).

<sup>#</sup> Present address: Secretaria de Saúde do Estado da Bahia, SESAB.

polar constituents, it was concluded that oils with higher levels of PUFA generally produce more polar compounds than other oils (15). The oxidation of sunflower oil at 70 °C and of soybean and rapeseed oils at temperatures varying from 190 to 280 °C showed the formation of several acids, hydrocarbons, and carbonyl compounds, among them saturated and unsaturated aldehydes (16).

The rate at which a given volatile degradation compound is emitted from the oil's surface during heating depends, among other factors, not only on the rates of its formation but also on its removing processes, such as degradation reactions the compound may undergo. These formation and removal mechanisms and their velocities are, on the other hand, dependent both on the heating conditions and on the chemical and structural characteristics of the molecule, such as the presence or not of unsaturation in its chain.

It is therefore clear that the understanding of how these parameters can affect the emissions of an oil, heated in the presence of oxygen, is very important to improve the heating process and to know how different substances are affected by it (13, 17).

In this study, palm and soybean oils were heated at the typical temperature used for frying foods (180 °C) through different times, in the presence of atmospheric oxygen, under continuous and intermittent heating conditions, and at three different surface to volume ratios, to study the influence of those parameters and the CC structure on the emission rates of the volatile aldehydes acetaldehyde, acrolein, propanal, butanal, hexanal, 2-heptenal, and 2-octenal. These oils were chosen because they are the most widely produced and consumed worldwide (18).

## MATERIALS AND METHODS

**Chemicals and Standards.** Solvents (HPLC grade) and chemicals (reagent grade) were purchased from Merck (Darmstadt, Germany) and Aldrich (Milwaukee, WI). Deionized organic-free water was prepared in a Barnstead NANOpure Diamond system (Dubuque, IA), followed by filtration through a 0.45  $\mu\text{m}$  Durapore HV membrane (Millipore, Milford, MA).

The 2,4-dinitrophenylhydrazones of the carbonyl compounds (DN-PHo) were prepared as described elsewhere (19, 20). Briefly, ethanol solutions of each carbonyl compound were added to an acidified ethanol solution of 2,4-dinitrophenylhydrazine (DNPHi) and set to rest at 25 °C for 30 min. The solid DNPHOs formed were then filtered, recrystallized when necessary, vacuum-dried in a desiccator, and finally stored protected from light and air humidity. These DNPHOs were used to prepare the calibration standards used for quantifying emissions from oils.

**Standard Solutions.** From an acetonitrile stock solution of the carbonyl hydrazones, previously prepared by weighing each DNPHo, the working standards were prepared, also in acetonitrile, for the following aldehydes in a concentration range from 0.1 to 1.4  $\mu\text{g mL}^{-1}$ : acetaldehyde, acrolein, propanal, butanal, (*E*)-2-hexenal, (*E*)-2-heptenal, and (*E*)-2-octenal. For hexanal, the concentration ranged from 0.5 to 7.0  $\mu\text{g mL}^{-1}$ .

**Prepare of the Sampling Cartridges.** The sampling cartridges (Sep-Pak Classic C18, 360 mg, Waters, Milford, MA) were impregnated with 2 mL of a 0.4% (w/v) DNPHi solution and put to dry in a gentle stream of nitrogen gas. After this, they were sealed with Teflon tape, wrapped with aluminum foil, and stored in a desiccator until sampling.

**Samples.** The palm and soybean oils were purchased in local markets. To minimize any heterogeneity from different suppliers, two composed samples were prepared by mixing five brands of soybean oil and four brands of palm oil, respectively. These samples were stored, under nitrogen flow, in amber glass bottles protected from light. Each

time aliquots of the samples were removed, the bottles were fluxed with nitrogen before capping to purge off traces of oxygen inside the bottles.

**Experimental Setup.** The experimental setup was adapted from the literature (4, 14) and was mounted according to the following. The oil sample was put into a 500 mL round-bottom glass flask and, while heating under continuous stirring, a flux (1 L  $\text{min}^{-1}$ ) of purified air was passed through the flask. During the experiments, oil samples were heated to 180 °C during 24 h, under continuous and noncontinuous conditions. In the noncontinuous condition, three heating cycles of 8 h each were intercalated by 16 h resting periods. The experiments in the continuous mode were carried out in triplicate and at three different *S/V* ratios, namely, 0.23, 0.43, and 0.77  $\text{cm}^{-1}$ , whereas in intermittent mode only the 0.43  $\text{cm}^{-1}$  ratio was tested.

The carbonyl compounds, emitted by oil samples during the heating experiments, were collected in two Sep-Pak cartridges connected in series, at a 0.2 L  $\text{min}^{-1}$  sampling flow rate for 5 min. For the continuous experiments, samplings were done at 1, 2, 3, 4, 5, 6, 7, and 24 h, whereas for intermittent experiments only one sampling was done 1 h after the beginning of each heating cycle. After sampling, the hydrazones were directly eluted with acetonitrile to an amber vial, and the final volume was taken to 5 mL before analysis.

**HPLC Analysis.** The carbonyl hydrazones were separated in an XTerra MS C18 column (2.1  $\times$  250 mm, 5  $\mu\text{m}$ , Waters) and determined in an LC-DAD-MS system Agilent 1100 (Agilent, Waldbronn, Germany) Bruker Esquire 3000 plus (Bruker, Billerica, MA), according to the following conditions: flow rate, 0.25 mL  $\text{min}^{-1}$ ; gradient of 0.1% formic acid in water (A) and acetonitrile (B), 40–100% B in 30 min, then 100% B for 6 min, returning to 40% B in 4 min, remaining for 5 min. The total run time was 45 min. By using a 2.1 mm column, it was possible to reduce by 75% the mobile phase consumption in each run, when compared to the conventional 4.6 mm columns. Quantitation of aldehydes was done by absorbance in the UV-vis at 365 nm, using external calibration curves. The results were first expressed as micrograms per milliliter of each CC in the extract solution, and these values were then converted to the emission rates in the oils, as micrograms per hour per liter. One sample of each oil and standard were run in the mass spectrometer to identify aldehydes and relate them with their retention times. The MS conditions were as follows: source, ESI; negative ionization; nebulizer pressure, 22.0 psi; dry gas flow, 10.0 L  $\text{min}^{-1}$ ; dry gas temperature, 300 °C; capillary, 4000 V.

## RESULTS AND DISCUSSION

Carbonyl compounds identified as significantly emitted by palm oil were acetaldehyde, acrolein, propanal, butanal, pentanal, hexanal, 2-heptenal, heptanal, 2-octenal, octanal, nonanal, and 2-decenal, whereas for soybean oil acetaldehyde, acrolein, hexanal, and 2-heptenal were the major emissions. Among these, only acetaldehyde, acrolein, propanal, butanal, hexanal, 2-heptenal, and 2-octenal were quantified during the experiments, because standards were available solely for these compounds.

In both oils, acrolein was the main aldehyde emitted in all conditions, with average emission rates ranging between 2580 and 41524  $\mu\text{g h}^{-1} \text{L}^{-1}$  for palm oil and between 11838 and 67372  $\mu\text{g h}^{-1} \text{L}^{-1}$  for soybean oil. Acrolein emission rates were followed in both oils by hexanal (559–6653 and 277–5798  $\mu\text{g h}^{-1} \text{L}^{-1}$ ), heptenal (146–4164 and 375–3250  $\mu\text{g h}^{-1} \text{L}^{-1}$ ), and acetaldehyde (218–2782 and 58–860  $\mu\text{g h}^{-1} \text{L}^{-1}$ ) for palm oil and soybean oil, respectively. Whereas the acrolein emission rates found in this study were in agreement with a previous work done with olive and canola oils (14), lower emission rates were found for hexanal, heptenal, and acetaldehyde.

Except for acrolein, the other aldehydes quantified in this study were, in general, more abundant in the emissions from palm oil. A possible explanation for this is the presence of carotenoids in the palm oil. The carotenoids are unstable compounds against heat and can be themselves a source for these carbonyls (21). The higher emissions of acrolein by soybean oil, when compared to palm oil,

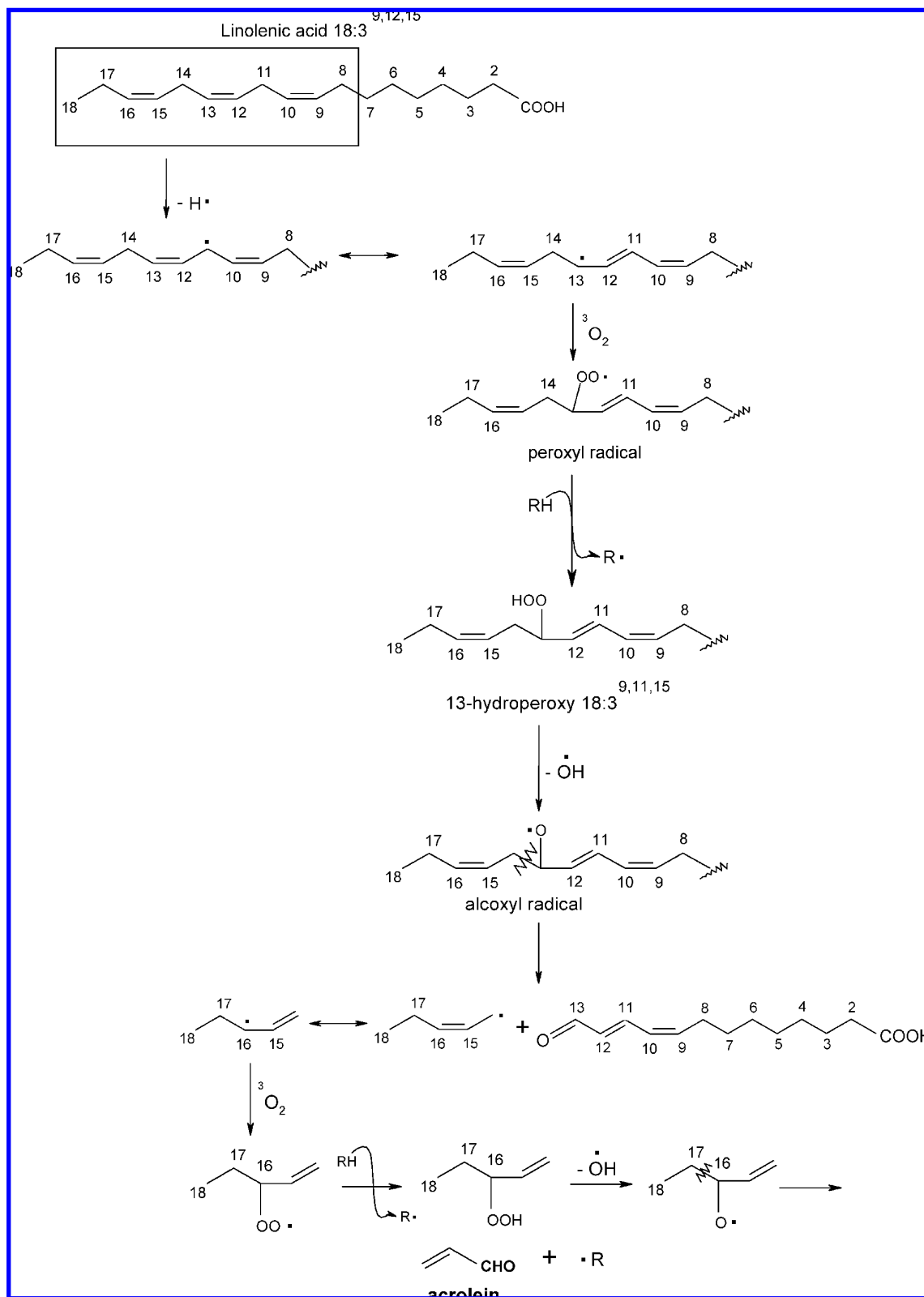


Figure 1. Proposed formation mechanism for acrolein from the oxidation of linolenic acid.

can be explained by its fatty acid composition profile, which is much richer in polyunsaturated fatty acids than the former. For example, soybean oil has, on average, 4–11% of linolenic acid and 44–62% of linoleic acid, whereas palm oil has, on average, <0.5% and 6.5–15% of these fatty acids, respectively. Figure 1 shows a mechanism proposed by us and based on previously published studies (22, 23) for the formation of acrolein from the oxidation of linolenic acid. This mechanism is based on a free

radical chain reaction, which begins with a hydrogen abstraction from an  $\alpha$ -methylene carbon, thus forming an allyl radical.

The emission rates as a function of the heating time and the  $S/V$  ratio are shown in Figures 2 and 3 for palm and soybean oil, respectively.

As can be seen from these figures they are, in general, directly related to the  $S/V$  ratio of the samples during the heating process. This seems obvious because the oxidative reactions depend on

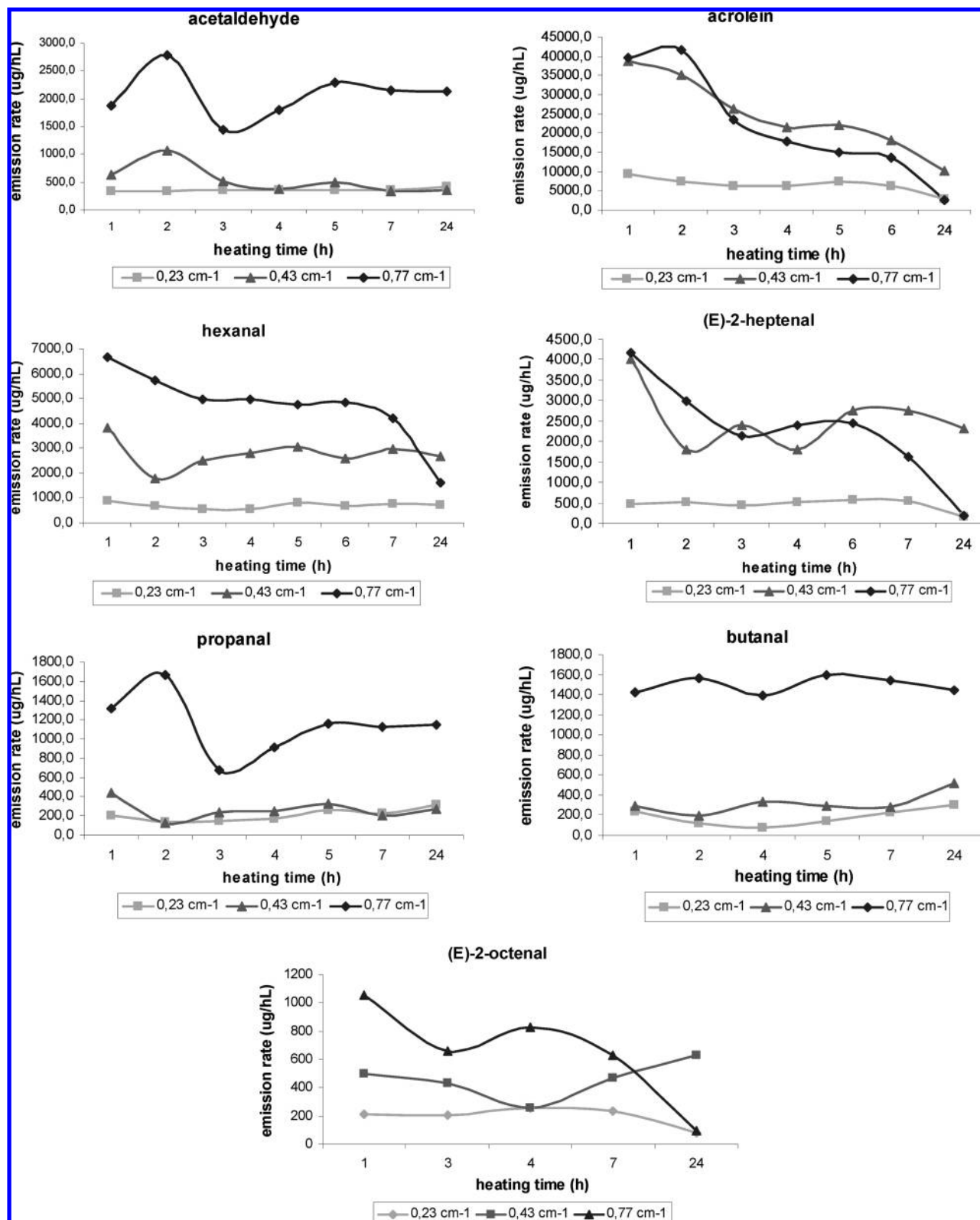


Figure 2. Emission rates of CC from palm oil during continuous heating at 180 °C, in the three *S/V* ratios.

the oxygen transfer from air to the oil (2, 5, 12) and, hence, on its surface that is exposed to the atmospheric oxygen. It should also be noted that the relative increases, as the *S/V* changed from 0.23 to 0.43 and to 0.77 cm<sup>-1</sup>, did not have the same behaviors for saturated and nonsaturated aldehydes. Indeed, for acetaldehyde, propanal, butanal, and hexanal the emission rates increased with the *S/V* ratio increase, although in some cases these increases had been more pronounced when the *S/V* rose

from 0.43 to 0.77 cm<sup>-1</sup>. For acrolein and 2-heptenal, on the other hand, the emission rates became close to each other or even suffered an inversion when the *S/V* changed from 0.43 to 0.77 cm<sup>-1</sup>.

A possible explanation for these different behaviors could be the double bond, present in both alkenals, which would be reacting with oxygen and other oxidative species formed during the process. Thus, as these two alkenals are formed, they are



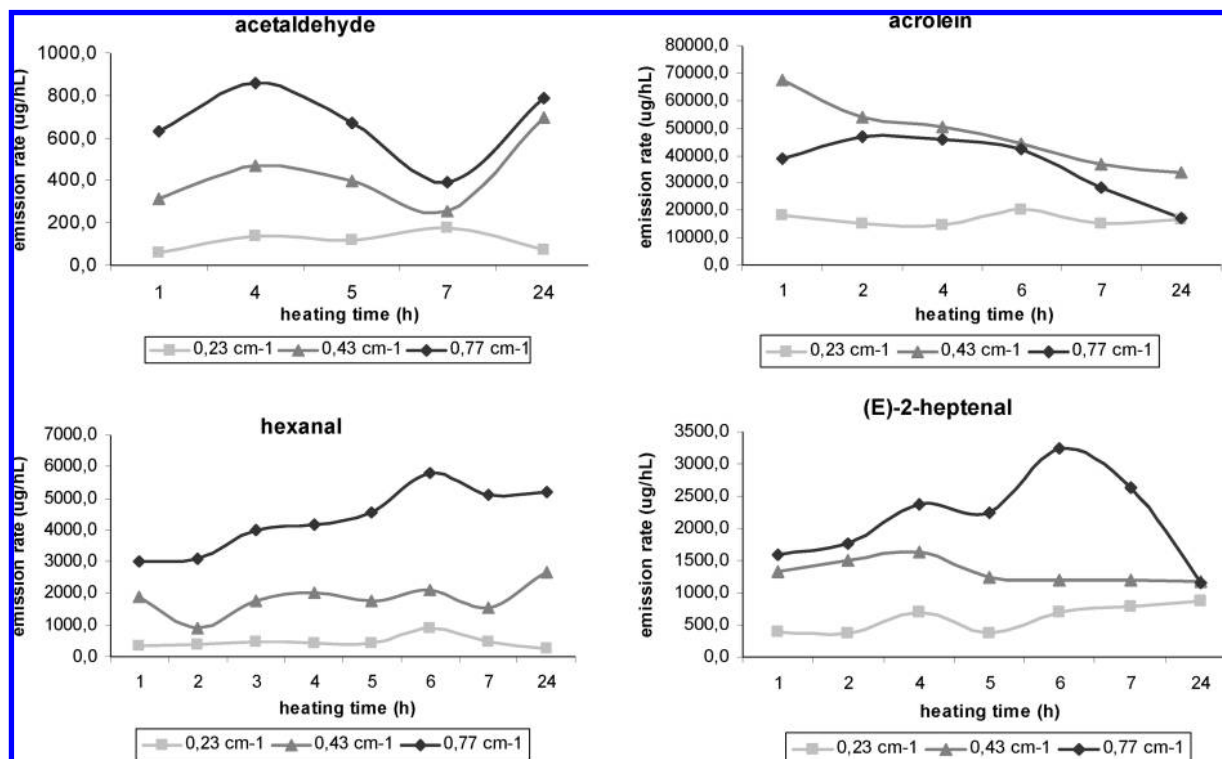


Figure 3. Emission rates of CC from soybean oil during continuous heating at 180 °C, in the three  $S/V$  ratios.

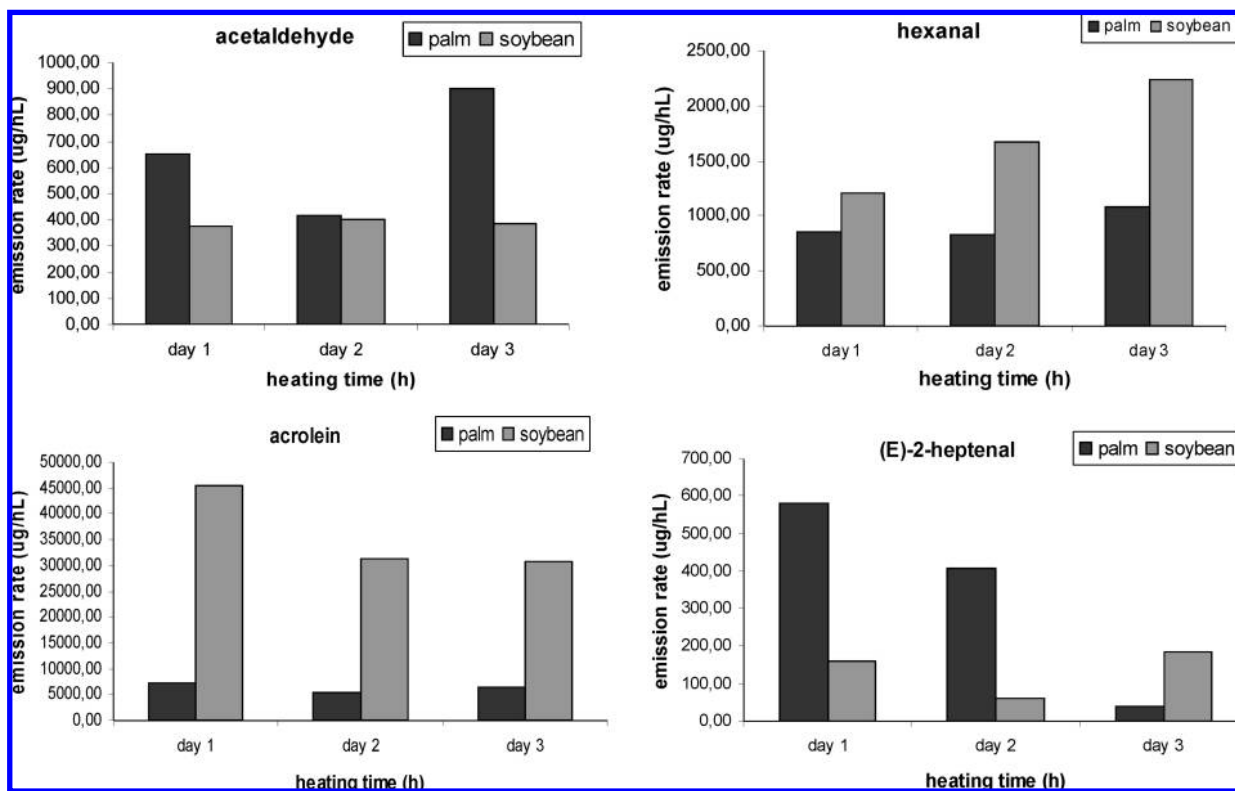


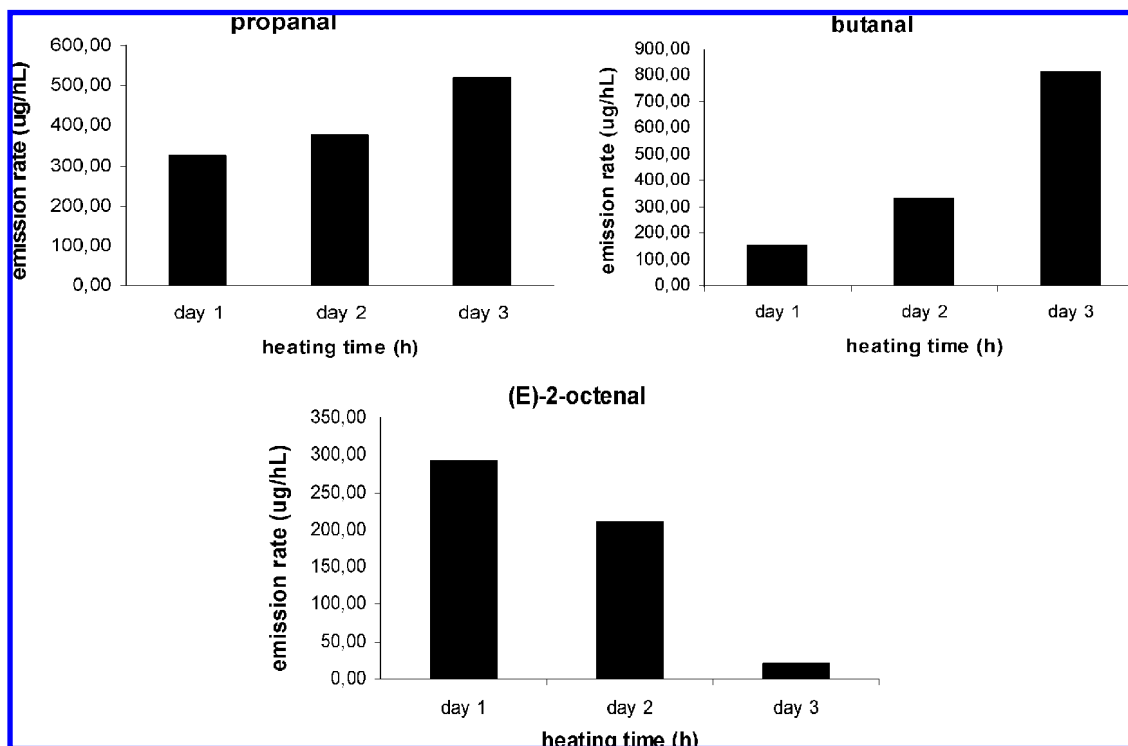
Figure 4. Emission rates of CC for palm and soybean oils during intermittent heating at 180 °C and  $S/V = 0.43 \text{ cm}^{-1}$ . (Samples were collected at the first hour in each day.)

also destroyed through these oxidation reactions. As the  $S/V$  became high, the oil surface exposed to the oxygen increased, leading to faster reaction rates.

The emission rates during intermittent heating are shown in **Figure 4** for CC found in palm and soybean oil, whereas **Figure 5** shows the emission rates for those carbonyl compounds found

only in the palm oil. All of the experiments in intermittent mode were done with a  $0.43 \text{ cm}^{-1}$   $S/V$  ratio.

The results for acrolein, acetaldehyde, and 2-heptenal were in accordance with that observed in the continuous experiments, in which soybean oil was, on average, a major source for the first one and palm oil for the last two. Hexanal, on the other



**Figure 5.** Emission rates of CC for palm oil during intermittent heating at 180 °C and  $S/V = 0.43 \text{ cm}^{-1}$ . (Samples were collected at the first hour in each day.)

hand, showed an inverse trend when compared with the continuous experiments, in which palm oil was, on average, a major source for this aldehyde.

A possible explanation for this inversion is that during the intermittent process, secondary oxidation reactions that may occur between two consecutive heating periods (e.g., with formed peroxides and dissolved oxygen) are favored. Because soybean oil has much more linoleic acid than palm oil, and this acid is the main precursor of hexanal when oxidized, soybean oil becomes thus the main source of hexanal.

As a rule, the emission rates of saturated carbonyl compounds increased during the three days of the experiments, whereas for unsaturated compounds there was a decrease during the experiments. According to the same reasons given above, secondary oxidation reactions that may occur between two consecutive heating periods are also favored in this case. Under these circumstances, nonsaturated compounds are more exposed to consuming processes, which take place through their double bonds. Those processes are as important as the formation processes, and they cause their emission factors to decrease, in an opposite manner to the saturated carbonyl compounds.

Finally, this work has shown that the oil's surface-to-volume ratio, the heating time, the heating process (continuous or intermittent), and the oil's fatty acid composition, as well as the characteristics of the carbonyl compounds formed, such as the presence or not of double bonds on their molecules, are important factors in the emission rates of the aldehydes studied. For both oils studied the acrolein emissions were significant, even after a short heating time. Nevertheless, this fact does not necessarily correspond to a high exposure of kitchen workers to this toxic compound, because it depends on other factors, such as the local degrees of exhaust and ventilation.

Possible measures to reduce the CC emissions could be, for example, the reduction of the oil's surface-to-volume ratios

employed and also the use of low concentrations of atmospheric oxygen during the heating process.

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