Furan formation as a function of pressure, temperature and time conditions in spinach purée

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Abstract

In recent studies, innovative high-pressure high-temperature processing (HPHT) has presented itself as an interesting alternative for furan reduction in sterilized, vegetable-based foods. In order to explain the observed furan reduction following HPHT treatment, furan formation was studied under a range of pressure, temperature and time conditions, using spinach purée as a case study. For all the treatments, no furan was detected during the dynamic heating-up phase, followed by a steady increase in furan concentrations at isothermal(-isobaric) conditions. The increase in furan concentrations at isothermal(-isobaric) treatment conditions could be adequately described by an empirical, zero-order model. A pressure level of 600 MPa did not affect the rate of furan formation in spinach purée, as opposed to the processing temperature and time. As a result, the reduced furan concentrations for HPHT processing could be explained by the faster heating and cooling rates, resulting in shorter processing times as compared with conventional retort processing.

Keywords

Furan; zero-order; thermal sterilization; high-pressure high-temperature processing; *Spinacia annuum*.

Chemical compounds studies in this article

Furan (PubChem CID: 8029)

1. Introduction

Furan (C_4H_4O) is a small organic molecule with high volatility. In 1995, furan was classified as 'possibly carcinogenic' to humans after it was proven to be carcinogenic in rats and mice (International Agency for Research on Cancer (IARC), 1995). A recent risk evaluation by the Joint FAO/WHO Expert Committee on Food Additives (2011) has indicated a human health concern for furan and consequently, actions should be taken to minimize exposure to an acceptable level. Sterilized, vegetable-based foods (jarred baby foods, ready-to-eat soups, sauces, etc.) are important contributors to the furan exposure of children and adults (European Food Safety Authority (EFSA), 2011). As a result, such foods can be considered an interesting target for furan mitigation. Based on the available literature (Crews & Castle, 2007; Blank, 2009; Anese, Manzocco, Calligaris, & Nicoli, 2013), three possible approaches for furan mitigation can be proposed: (i) lowering the amount of furan precursors and/or changing the reaction pathways by adding or removing substances from the product, (ii) optimization of conventional heating processes or application of an alternative processing technique (e.g. high pressure processing) and (iii) post-process reduction of the amount of furan formed (e.g. ionizing radiation, vacuum treatment). With regard to the second approach, high-pressure high-temperature processing (HPHT) has presented itself as an interesting alternative for furan reduction in conduction-heated foods. HPHT processing is an innovative processing technology that has been given a lot of research attention in the recent search for foods with high-quality properties. The application of the process parameter pressure enables faster heating and cooling rates, which can result in shorter processing times compared with conventional retort treatments (Cheftel, Hayashi, Heremans, & Masson, 1992). Furthermore, high pressure can have decelerating or accelerating effects on the rate constant of chemical reactions (Cheftel et al., 1992), thereby creating a new dimension for process design and optimization.

The potential of HPHT processing for furan reduction in sterilized, vegetable-based foods, was investigated in a recent study by Palmers, Grauwet, Kebede, Hendrickx, & Van Loey (2014). A wide range of vegetable purées was subjected to a HPHT treatment (117 °C, 600 MPa) and a conventional thermal treatment (117 °C, 0.1 MPa). To obtain a fair comparison for the process impact of both treatments, an equivalent, industrially relevant process value ($F_{121.1\,°C}^{10\,°C}$ = 5 min) was targeted. Following the treatments, the HPHT-treated vegetable purées had clearly lower furan concentrations (1-2 ng/g purée) than the thermally treated purées (mean concentrations of 7-8 ng/g purée). Similar observations were also made by Sevenich et al. in fish (2013) and in vegetable-based baby food systems (2014). The same authors even showed that it is possible to scale-up this technology to a pilot scale, whilst keeping the same reduction of furan concentrations (Sevenich et al., 2015). Nevertheless, a lot of scientific, technical and legislative issues are still to be overcome before HPHT processing can serve as a real alternative for commercial sterilization processes (Rastogi, Raghavarao, Balasubramaniam, Niranjan, & Knorr, 2007; Balasubramaniam & Farkas, 2008).

To this day, the specific mechanism of furan reduction during HPHT processing remains unclear. All the above-mentioned studies aimed to compare the integrated effect of the process parameters pressure, temperature and time on the furan concentrations of various heat-treated foods. As a result, it was not possible to attribute the observed furan reduction for HPHT processing to the shorter processing times, a possible decelerating effect of high pressure on the rate of furan formation, or a combination of both. Moreover, there is still a lack of quantitative data on the effects of the processing temperature and time for furan reduction during conventional thermal sterilization of vegetable-based foods. To address both research questions, furan formation was studied over a range of pressure, temperature and time conditions, using spinach purée as a case study. Spinach is a commonly used ingredient of vegetable-based products. It contains almost all known furan precursors and has been shown to be a vegetable type susceptible to furan formation (Palmers et al., 2014). Information on the effects of the individual processing variables for furan formation in spinach purée, is a logical next step towards process control and optimization in other vegetable-based foods (Grauwet et al., 2014).

2. Material and methods

2.1.Preparation of the spinach purées

Fresh spinach (*Spinacia annuum* 'Hudson') was bought at a local supplier. Petioles were removed and the leaves were carefully washed, before vacuum-packing in low-density polyethylene bags. To assure that all the changes observed during thermal and HPHT processing were chemical, the vegetables were blanched at 95 °C for 8 min in a water bath (WBU 45, Memmert, Schwabach, Germany). After blanching, the plastic bags were cooled in iced water for 10 min and stored in a freezer at -40 °C. Prior to thermal or HPHT treatment, the frozen spinach was thawed in a cold room at 4 °C and blended (B-400, BÜCHI, Flawil, Switzerland) to obtain a homogeneous purée.

2.2.Isothermal treatment

Stainless steel tubes (13 mm inner diameter, 16 mm outer diameter, 150 mm length) were completely filled with spinach purée (no headspace), tightly closed and immersed in an oil bath (Grant Instruments, Royston, UK) preset at the desired processing temperature. The thermal treatments were performed under isothermal conditions, at three different temperatures (110, 117 and 124 °C) as a function of time. The temperature of the purées was monitored with type-T thermocouples (Thermo Electric Company, Balen, Belgium), connected to an Ellab E-val temperature registration system (Ellab, Hilleroed, Denmark). As an example, the temperature-time profile of the isothermal treatment with a holding time of 35 min at 117 °C is represented in **Fig. 1** (bold dark line). Following treatment, the samples were immediately transferred to iced water to cool down the samples. Subsequently, treated samples were emptied in a cold room at 4 °C and transferred to small volume polyethylene terephthalate tubes with a polyethylene cap. The tubes were frozen in liquid nitrogen and stored at -40 °C until analysis.

2.3.Isothermal-isobaric treatment

Teflon sample holders (diameter 12 mm, length 85 mm) were completely filled with spinach purée (no headspace), closed with a movable stopper, and vacuum-packed with double plastic bags. HPHT treatments were performed in a laboratory-scale 6-vessel equipment (vessel diameter 2 cm, volume 43 ml, Resato, Roden, Netherlands), provided with computer-controlled pressure build-up and data logging software for pressure and temperature. Propylene glycol (PG fluid, Resato, Roden, Netherlands) was used as a pressure medium. The treatments were performed under isothermal-isobaric conditions, at two different temperatures (110 and 117 °C) and a pressure level of 600 MPa as a function of time according to a protocol of Grauwet, Van der Plancken, Vervoort, Hendrickx, & Van Loey (2010). Using only compression heating, product temperatures cannot be raised to the desired processing temperatures. Therefore, after loading the tubes into the preheated high-pressure vessels, the samples were heated to an experimentally determined temperature (72 and 75 °C, respectively). When this temperature was reached, the pressure build-up started. Two consecutive stages could be identified: (1) an instantaneous pressure increase from 0.1 to 150 MPa; (2) a further pressure increase to 600 MPa at a rate of 10 MPa/s. After reaching 600 MPa, the individual vessels were isolated, and an equilibration time of 1 min was taken into account. At the selected holding times, the pressure was released from the vessels, which was accompanied by a fast temperature drop inside the product (decompression cooling). An example of the temperature-time profile (bold light line) and the pressure level (dashed light line) for the isothermal-isobaric treatment with a holding time of 35 min at 117 °C and 600 MPa is represented in **Fig. 1**. Following treatment, the samples were immediately transferred to iced water. To minimize possible losses of furan during handling of the samples, all HPHT treated samples were analyzed within 24 h after the treatment was finished.

2.4.Quantitation of furan

Quantitation of furan was performed via isotope dilution assay as described by Palmers et al. (2014), using furan-d_4 as an internal standard. For sample preparation, 2.5 g of the thermally or HPHT-treated spinach purées was weighed into an 10 ml headspace vial with a PTFE/silicone septum seal. The purée was diluted with 2.5 ml of a saturated NaCl solution, 100 µl of furan-d_4 (98%, Sigma-Aldrich, Saint Louis, Missouri) working solution (ca. 0.05 µg/ml in deionized water), and deionized water to obtain a standardized total volume of 6 ml. Furan was extracted by solid phase microextraction (SPME), using a 75 µm carboxen/polydimethylsiloxane fiber (Supelco, Bellefonte, Pennsylvania) which was exposed to the headspace of the samples at 30 °C for 15 min. The analyses were carried out using an Agilent 7890A gas chromatograph and an Agilent 5975C mass spectrometer (Keysight Technologies, Santa Rosa, California), equipped with HP-PLOT Q column (30 m × 320 µm, 20 µm film thickness, Keysight Technologies, Santa Rosa, California) using helium as the carrier gas at a constant flow rate of 2 ml/min. Mass spectra were obtained by electron ionisation (EI) at 70 eV, in the combined SCAN and SIM mode. The selected ions monitored were m/z 68 (quantifier) and 39 (qualifier) for furan and m/z 72 (quantifier), 44 and 42 (both qualifier) for furan-d_4. For quantitation, a calibration curve of furan (>99%, Sigma-Aldrich, Saint Louis, Missouri) was prepared in the blanched spinach purée, covering the concentration range of 0-50 ng/g purée. The decision limit and the detection capability of the procedure were 1.15 ng/g purée and 1.86 ng/g purée, respectively. Each sample was analyzed in duplicate.

2.5. Analysis of the kinetic data

Furan formation was kinetically modeled as a function of time and temperature (at two particular pressure levels of 0.1 and 600 MPa). For a detailed discussion on the general principles of kinetic modeling, the reader is referred to the work of van Boekel (2009). In general, the formation rate of a process-induced compound can be described by the rate law (Equation 1), where r is representing the rate of the reaction, A the concentration of the compound at holding time t, k the reaction rate constant at the selected pressure and temperature levels, and n the order of the reaction. When studying kinetics under isothermal(-isobaric) conditions, k can be considered constant in time and the general rate law can be integrated with respect to treatment time. The temperature-dependency of the reaction rate constant k can often be expressed by the Arrhenius equation, in terms of activation energy E_a (Equation 2), where k_T and k_{Tref} represent the reaction rate constant at the selected processing temperature T and the reference temperature T_{ref}, respectively, and R the universal gas constant (8.314 J/K.mol).

$$r = \frac{dA}{dt} = kA^n \qquad (1)$$

$$k_T = k_{Tref} exp\left(\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (2)$$

Kinetic modeling of the furan concentrations in the treated spinach purées was performed in two steps. As mentioned above, furan concentrations were analyzed in duplicate. For each time moment, both data points were entered into the modeling procedure. First, a suitable kinetic model was selected by visual inspection of the different concentration plots, the parity plots and the residual plots, and by the calculation of R^2_{adjusted}. Second, the corresponding kinetic parameters were estimated using one-step nonlinear regression (SAS version 9.4, Cary, North Carolina).

3. Results and discussion

3.1. Kinetics of furan formation during isothermal treatments

In order to quantify the effect of the processing temperature on the rate of furan formation, spinach purée was thermally treated at three different temperatures (110, 117 and 124 °C). At all temperatures, no furan was detected during the dynamic heating-up phase of the treatment. The furan concentrations started to increase at isothermal conditions. Therefore, the rate of furan formation was only compared under the latter conditions (**Fig. 2**). From these results, the rate of furan formation was clearly higher at higher processing temperatures. Depending on the tested treatment conditions, maximum furan concentrations up to 8-12 ng/g spinach purée were reached. These concentrations are comparable to the furan concentrations reported in literature sources based on model systems (Fan, 2005; Owczarek-Fendor et al., 2010; Owczarek-Fendor et al., 2012). Compared to commercially available, vegetable-based products (mean concentrations up to 48-49 µg/kg, depending on the product) (European Food Safety Authority (EFSA), 2011; US Food and Drug Administration (FDA), 2009), the concentrations were still relatively low. The differences in furan concentrations might be explained by differences in the matrix composition (e.g. absence of oils or fat) and by the fact that in food industry, products are often exposed to higher processing intensities (larger volume of the products, thus resulting in a higher degree of overprocessing) than in the present study.

The results of the isothermal treatments clearly indicated the importance of the processing temperature and time for the furan concentrations of vegetable-based foods. Although not monitored in the present study, the increased furan formation at high processing temperatures could most probably be explained by the increased degradation of both primary (e.g. sugars, ascorbic acid and carotenoids) and secondary precursors (e.g. starch) for furan in foods. To quantify the effect of the processing temperature on the rate of furan formation in spinach purée, the results were analyzed using kinetic modeling. To simplify the analysis, the induction step prior to obtaining isothermal treatment conditions was not taken into account for the modeling procedure. At isothermal conditions, the increase in furan concentration was adequately described by an empirical, zero-order model (**Fig. 2**). Zero-order reactions are rather frequently observed in foods, especially for formation reactions when the amount of product formed is only a small fraction of the amount of precursors present (as is the case for furan formation). In such a case, the reactant concentration remains effectively constant throughout the observation period, and hence the rate appears to be independent of the concentration (van Boekel, 2009).

All the kinetic parameters of the present study were estimated by means of nonlinear one-step regression. The temperature dependence of the reaction rate constants could be described with the Arrhenius law. Model evaluation was based on visual inspection of the parity and residual plots (graphs not shown) and by the calculation of R^2_{adjusted} (0.958), which all indicated a good fit of the selected model. The reaction rate constant at a reference temperature of 117 °C (k_{Tref}) and the corresponding activation energy (E_a) are represented in **Table 1**. The reaction rate constants at each other processing temperature (0.035, 0.071 and 0.142 ng/g purée/min, at 110, 117 and 124 °C, respectively) can be calculated from these reference values. If the processing temperature was increased with 7 °C, the reaction rate constants approximately doubled. The observed temperature-dependency of the reaction rate constants was therefore very comparable to the values reported for nutrient degradation reactions in literature. In general, these reaction rate constants seem to double for every 10 °C temperature increase, as opposed to microbial inactivation rates for example, that increase tenfold for the same temperature increase (van Boekel, 2009). The activation energy of furan formation amounted to 127.6 kJ/mol. Also this value is at least in the same range as activation energies for other chemical reactions (van Boekel, 2009). It should be realized that the formation of furan is reflecting more than a single reaction, since the formation is the overall result of various reaction pathways and interactions. Consequently, one has to be careful with the application of these apparent kinetic parameters for process optimization in vegetable-based food systems (which was outside the scope of the present study). In the literature, there is only one study investigating furan formation in a kinetic manner. Mogol & Gökmen (2013) used the approach of multiresponse modeling to obtain insight into the furan formation from ascorbic acid, at elevated temperatures and in a model system under low moisture conditions. However, because of the distinctly different experimental setup of the present study, a comparison of the kinetic parameters obtained in both studies is pointless.

3.2.Kinetics of furan formation during isothermal-isobaric treatments

The effect of the processing temperature on the rate of furan formation was also investigated at one elevated pressure level of 600 MPa. Spinach purée was HPHT treated at two different temperatures (110 and 117 °C). No HPHT treatment was performed at 124 °C, because the isothermal-isobaric conditions, desired for kinetic modeling, were difficult to maintain at this high temperature. At both temperatures tested, no furan was detected during the dynamic heating-up phase of the treatment. After obtaining isothermal-isobaric conditions, it took another 20 min to detect furan. Then, the furan concentrations steadily increased until the end of the treatments (**Fig. 3**). The rate of furan formation was clearly higher at a higher processing temperature. The maximum furan concentrations (8-10 ng/g spinach purée) were very comparable to the maximum concentrations observed after the isothermal treatments.

Analogous to the isothermal treatments, the results were analyzed using kinetic modeling. The increase in furan concentration at isothermal-isobaric conditions was again adequately described by an empirical, zero-order model (**Fig. 3**), as could be concluded from a visual inspection of the parity and the residual plots (graphs not shown). At both temperatures, the reaction rate constant was estimated using linear regression (**Table 1**). The values of R^2_{adjusted} confirmed a reasonably good fit for both models (0.927 and 0.794, for the zero-order models at 110 and 117 °C, respectively). Like for the isothermal treatments, the rate of furan formation at 117 °C was approximately two times higher than the rate at 110 °C. In other words, the temperature-sensitivity of furan formation in vegetable-based products did not seem to be affected by the application of the process parameter pressure. Because the isothermal-isobaric treatments were only performed at two processing temperatures, no activation energy could be estimated under conditions of elevated pressure. As explained in the introduction, the literature on the furan formation during HPHT treatments of foods is scarce. Palmers et al. (2014) and Sevenich et al. (2014) have observed clear furan reductions in vegetable-based products, following HPHT treatments aiming at industrially relevant process values of 5 and 7 min, respectively. However, the specific experimental set-up of both experiments did not allow to obtain an insight into the effects of the parameters pressure, temperature and time separately. By using a kinetic modeling approach, the present study was able to quantitatively describe the effect of processing temperature and time on the rate of furan formation in thermally and HPHT-treated spinach purées. The individual effect of pressure will be discussed in the next section.

3.3. Effect of pressure on the rate of furan formation during HPHT treatments

The effect of high pressure on the rate of furan formation in vegetable-based foods was investigated by comparing the increase in furan concentrations of the thermally and the HPHT-treated spinach purées at fixed processing temperatures (**Fig. 4**). The isothermal(-isobaric) treatments applied in this study had two processing temperatures in common (110 and 117 °C). At both temperatures, the HPHT-treated spinach purées had a slightly lower furan concentration than their thermally treated equivalents. However, the rate of furan formation was very similar for both types of spinach purées, as confirmed by the results of the kinetic modeling procedure (**Table 1**). At isothermal(-isobaric) conditions, the pressure level was the only factor differentiating between the thermal and the HPHT treatments, which allowed to obtain clear insight into the individual effect of this process parameter. Given the large number of data points and the long treatment times involved for both types of treatment, it could be concluded that a pressure level of 600 MPa had no observable effect on the rate of furan formation in spinach purée. As a consequence, the levels of furan concentration could be related to the integrated effect of the processing temperature and time, parameters for which the effect on furan formation was clearly demonstrated in the sections above. In agreement with this explanation, the differences in furan concentrations of the thermally and the HPHT-treated spinach purées could be explained by a different temperature-time history during the dynamic heating-up phase prior to obtaining isothermal(-isobaric) treatment conditions. As expected based on the lower furan concentrations, the HPHT-treated purées were characterized by a shorter heating-up phase as compared with the thermally treated purées, thus resulting in a small reduction of the thermal load applied to the product (**Fig. 1**).

The fact that pressure, in contrast to the processing temperature and time, had no effect on the rate of furan formation in spinach purée, has important implications for the understanding of furan formation in vegetable-based foods. As mentioned in the introduction, HPHT processing has shown great potential for furan reduction in sterilized vegetable purées (Sevenich et al., 2014; Palmers et al., 2014). However, the mechanism of furan reduction could not be fully elucidated due to a lack of quantitative data on the effect of the individual processing variables pressure, temperature and time on the rate of furan formation in vegetable-based foods. On the one hand, HPHT processing was characterized by faster heating and cooling rates, resulting in a reduction of the thermal load applied to the product. On the other hand, pressure might have a decelerating effect on the rate of furan formation. Based on the results of the present study, the latter option may be discarded. It should be noted however, that high pressure can still have an effect on the constituting reaction steps. Furan formation is the result of a complex network of reactions. Several furan precursors are known to be affected by high pressure, as reported in the literature. For example, the Maillard reaction appears to be reduced (De Vleeschouwer, Van der Plancken, Van Loey, & Hendrickx, 2010), while the oxidative thermal degradation of ascorbic acid and unsaturated fatty acids are enhanced by HPHT processing (Kebede et al., 2013; Verbeyst, Bogaerts, Van der Plancken, Hendrickx, & Van Loey, 2013). The contribution of each individual precursor to the total furan concentration in the product is still under research. However, as both reducing and enhancing effects have been reported, the overall effect of high pressure on the rate of furan formation in spinach (and other vegetable-based foods) might become apparently nonexisting. In the context of furan mitigation, the major advantage of HPHT processing appears to be the faster heating and cooling rates. These rates can be obtained because of the conversion of compression work into internal energy and vice versa. The application of high pressure therefore allows for a fast and nearly uniform temperature change of the product. For some products (often slow, conduction-heated foods), the reduction of the thermal load applied to the product is large enough to result in a measurable quality improvement, as is the case for the furan concentrations. However, it goes without saying that HPHT processing cannot serve as a real alternative for the sterilization of vegetable-based foods, as long as the general impact on other important food safety and quality attributes is not fully established.

4. Conclusions

In recent studies, innovative HPHT processing has presented itself as an interesting alternative for furan reduction in sterilized, vegetable-based foods. In order to explain the observed reduction in furan concentrations following HPHT treatment, furan formation was investigated under a range of pressure, temperature and time conditions, using spinach purée as a case study. An empirical, zero-order model was an adequate way to describe the increase in furan concentrations at isothermal(-isobaric) treatment conditions. A pressure level of 600 MPa had no overall effect on the rate of furan formation in spinach purée, as opposed to the processing temperature and time. As a result, the furan concentrations of vegetable-based foods can be related to the integrated effect of both process parameters. Based on the results of the present study, the observed reduction in furan concentrations following HPHT treatment can be explained by the faster heating and cooling rates, resulting in shorter processing times for HPHT processing as compared with conventional retort processing. This way, HPHT processing can be considered an application of the high-temperature short-time principle to conduction-heated foods. To this day, HPHT processing is not available as a commercial sterilization technology. Next to technical and legislative issues, the impact of HPHT processing on different food safety (e.g. microbial target organism, other contaminants) and quality attributes (e.g. color, aroma) should be further investigated, before HPHT processing can serve as a real sterilization alternative. For many products, conventional thermal sterilization will remain the standard preservation technology. For such products, furan mitigation might be challenging, both because of the complexity of the food matrix and microbial safety standards to be guaranteed. However, other advanced or innovative processing technologies (e.g. microwave heating, ohmic heating) aiming at a reduction of the thermal load might take advantage of the same principle as for HPHT processing to reduce the furan concentrations of vegetable-based foods.

Acknowledgments

Stijn Palmers and Miete Celus are funded by the Agency for Innovation by Science and Technology in Flanders (IWT), Tara Grauwet by the Research Foundation Flanders (FWO), and Biniam T. Kebede by the KU Leuven Research Fund.

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Table 1. Estimated kinetic parameters based on a zero-order model describing furan formation in spinach purée during isothermal (0.1 MPa) and isothermal-isobaric (600 MPa) treatments.

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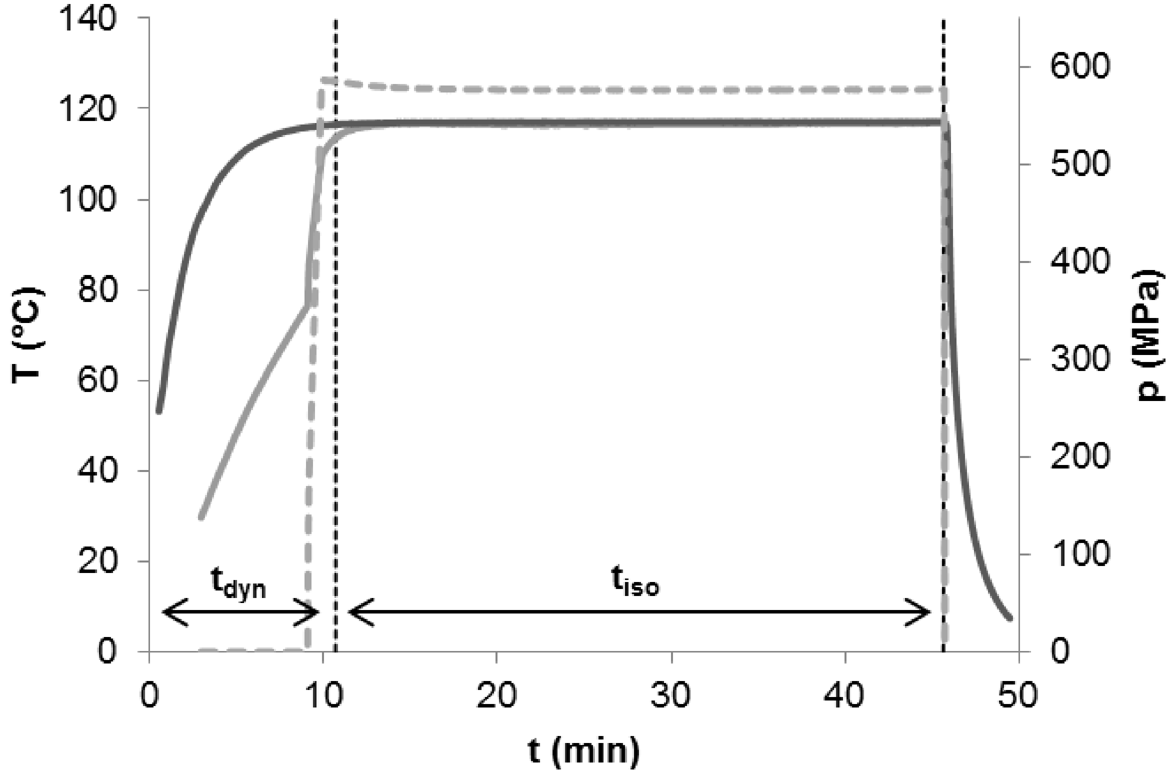

Fig. 1. Overlay of the temperature-time profiles for the spinach purées during thermal (bold dark line) and HPHT (bold light line) treatments at a processing temperature of 117 °C, with an isothermal(-isobaric) treatment time of 35 minutes. The pressure level (dashed light line) during the HPHT treatment is also represented. For each treatment, two consecutive treatment steps can be distinguished: the dynamic heating-up phase (t_{dyn}) followed by the holding time at isothermal(-isobaric) conditions (t_{iso}).

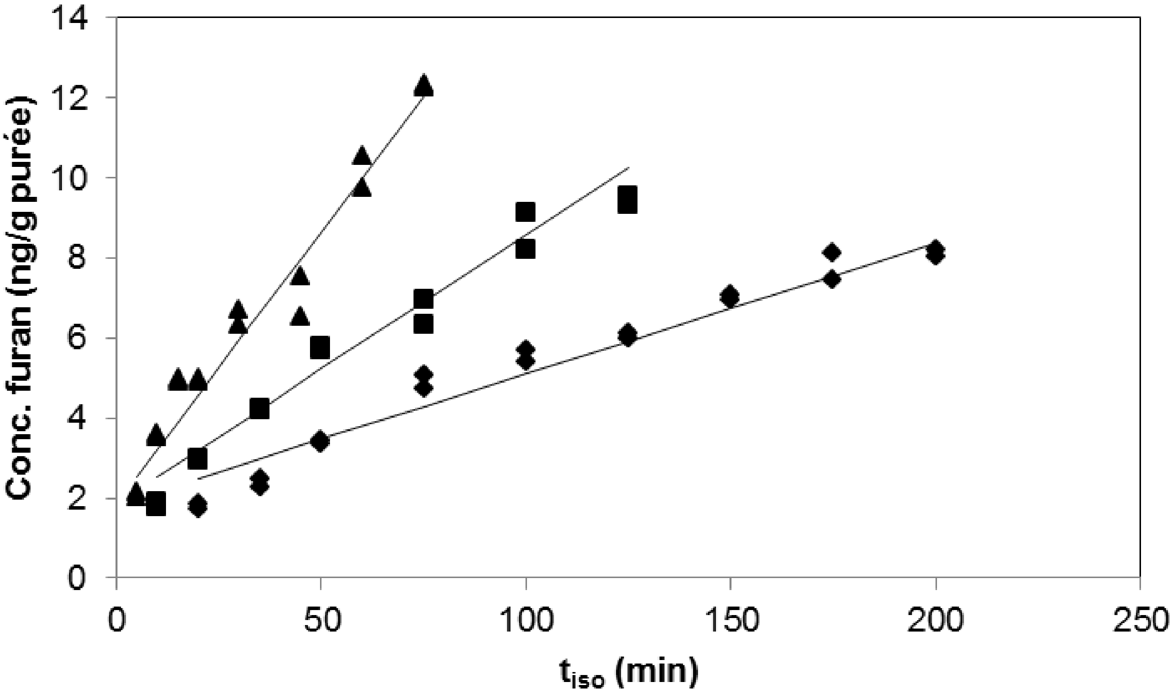

Fig. 2. Concentration of furan as a function of isothermal treatment time at a pressure of 0.1 MPa and a temperature of 110 (◆), 117 (■) and 124 °C (▲). The full lines represent furan concentrations predicted by a zero-order model, while the experimental data are represented by the symbols.

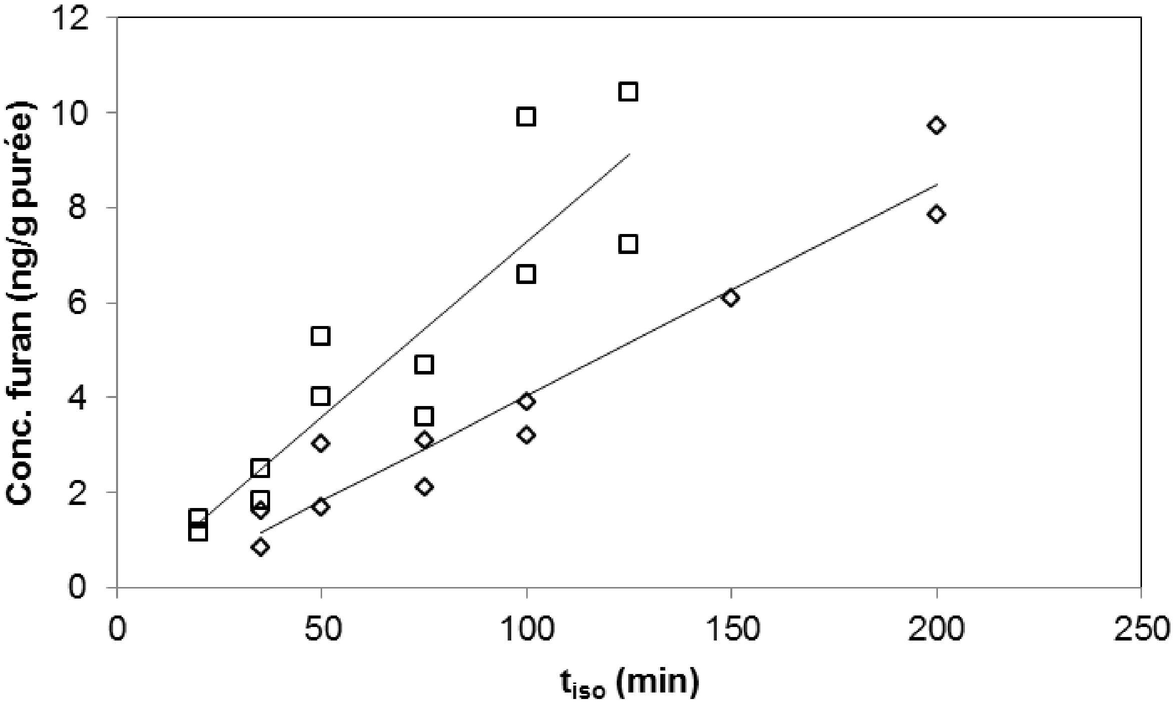

Fig. 3. Concentration of furan as a function of isothermal-isobaric treatment time at a pressure of 600 MPa and a temperature of 110 (◇) and 117 °C (□). The full lines represent furan concentrations predicted by a zero-order model, while the experimental data are represented by the symbols.

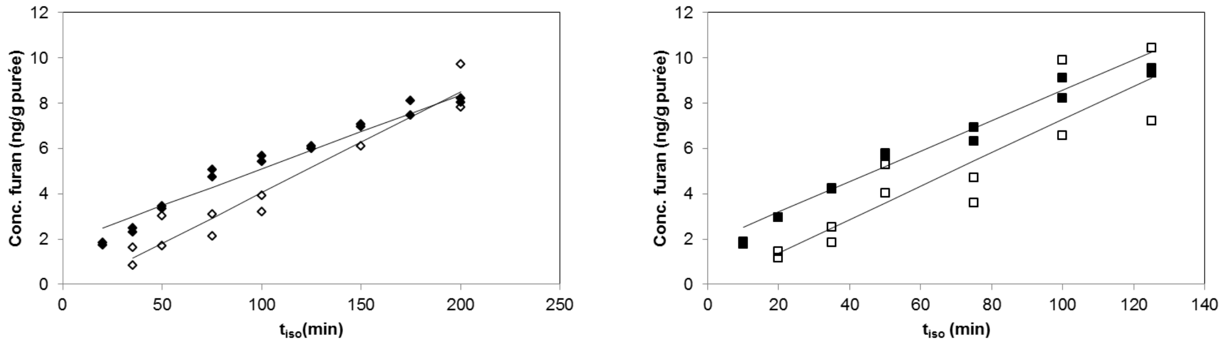

Fig. 4. Overlay of furan concentrations as a function of isothermal(-isobaric) treatment time for the thermal and HPHT treatments at 110 (diamonds, left) and 117 °C (squares, right). The filled symbols represent furan concentrations at 0.1 MPa, the empty symbols represent furan concentrations at 600 MPa. The full lines represent the fitted zero-order model.