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Abstract:

The purpose of the article is to implement a holistic concept namely Quality by Design (QbD) approach for assessment of deep frying of potatoes chips. Critical quality attributes (CQAs), critical process parameters (CPPs) and quality target parameters (QTPs) were identified and measured all along the chips processing chain in 98 independent experiments. Temperature, time and oil quality usually used in the food industry were applied. Multilinear regression (MLR) was conducted to identify the variables (CQAs and CPPs) that could explain variation of the QTPs. An aggregation of significant QTPs was also performed in order to determine a single value that could express final products quality coupled to MLR analysis. It was possible to identify the main CQAs and CPPs that can explain the variation of some QTPs (colour a*, "flavour roast" sensory attribute, pentylfuran content and acrylamide content) as well as aggregated data.

Keywords: Quality by Design, Potatoe Chips, Deep frying, Multilinear regressions, temperature

1. INTRODUCTION

Food consumer and retailer expectations are incessantly increasing, market requires safe and nutritious food that looks appetizing, tastes good, at an affordable price and with a minimal environmental impact. To achieve consistency in all the product properties the process conditions (path to endpoint or process signature) must also be kept under statistical control [Kourti, 2006]. However, food materials are complex biological matrices, and the variability introduced by the sequence of unit operations in food processing directly influences the compositional and sensorial properties as well as the safety and the shelf-life of the final food products. To reduce this variability, the strategies based on Quality Assurance can be quite effective but are expensive and not flawless (Chen et al., 2011).

Therefore, the food producers must frequently manage poor repeatability of food quality attributes and batch failures; unsuitable or noncompliant batches must be discarded or reworked with high additional costs. To overcome these problems, the food industry is trying to shift to a novel holistic concept, the Quality by Design (QbD), which initially has been implemented by the pharmaceutical industry in 2004 by the United States Food and Drug Administration (FDA, 2004; Bakeev, 2010; van den Berg et al. 2013; Tajmmal Munir et al. 2015). The QbD hypothesis is that the quality of the food products should be incorporated during their development by precisely designing and controlling the process, and not by post-production quality testing (Rathore & Kapoor, 2017). Adoption of such innovative process concept can also give a broader view of the parameters to be optimized to ensure safe and high-quality food products (Cullen et al. 2014).

Examples of QbD applications in the food industry are increasing, even if examples of real industrial during-production monitoring are rare in the scientific literature because it might reveal confidential product and process information. In many cases there is, however, a clear need to bridge the gap between the many promising scientific reports and actual use of these methods in the food industry (van den Berg et al. 2013; Panikuttira & O'Donnell 2018).

Among the industrial food processes, deep-frying is a common, but complex, multifunctional unit operation for fast dewatering, texturing or cooking foods, which simultaneously involves heat and mass transfer. One of the most widespread fried products are the potato chips, whose production embraces different steps, such as washing and peeling of raw materials, slicing, blanching and dewatering, etc. Deep frying is considered the more critical step, because the quality and safety of the final fried products are influenced by many factors, such as the nature and composition of fried materials, the combination of processing time and temperature, the heating profile, the oxidation status of frying oil, etc. (Rojo & Perkins, 1987; Vitrac et al., 2003; González-Martínez et al., 2004; Chatzilazarou et al., 2006; Romani et al., 2009; Kalogianni et al., 2010; Zhang et al., 2012; Kalogianni et al. 2017).

The main objective of the present study is to establish a Quality by Design approach in order to identify main quality parameters of the final products related with safety, taste and colour and to identified the useful quality and process parameters that can explain variation during production of deep-fried potatoes "chips". Another objective is the evaluation of suitable data aggregation strategies that could predict the quality and safety parameters of the final product.

2. Material and Methods

2.1 Fresh potatoes and frying oils

Homogenous 30 kg batches of potatoes (cultivar Agria) suitable for deep frying (Yang et al., 2016) were provided by Frufesc (Disbesa Grup, Barcelona, Spain) during a period of 5 month (from October to February). Each batch was used to carry out five frying experiments during the same working day. The potato batch was randomly divided in 5 aliquots of 5 kg each, which were processed sequentially along the same working day. Commercial fresh and exhaust sunflower oil, commonly used in the industry were both provided by an industrial manufacturer of potatoes chips (Grupo Siro, Palencia, Spain).

2.1 Frying equipment

The frying process was carried out with a continuous fryer model Frymatic24 (Nilma S.p.a., Parma, Italy), with a maximum capacity of 40 kg/h, and equipped with an original Distribute Temperature Sensor (DTS) made by the Institute of Photonic Sciences (ICFO, Casteldefelds, Spain). The DTS probes were based on Fibre Bragg Gratings (FBG) written in two optical fibres. Each of the two probes consisted of five single FBGs, equi-spaced (15 cm) on the same optical fibre, protected by a stainless tube and connected only at one end, on an armoured patch-cord terminated with a FC/UPC connector. Therefore DTS probes recorded simultaneously, each second, oil temperature in ten points along the frying tank (Figure 1). Temperature values recorded by the two probes in the same position along the tank were aggregated to define five temperature zones called E, M1, M2, M3 and Ex, where “E” zone corresponded to the entrance of the potatoes in the frying tank, and the “Ex” zone corresponded to the exit (Figure 1). Oil temperature was measured before starting (TO_{av}) and during ($TC°_{E}$, $TC°_{M1}$, $TC°_{M2}$, $TC°_{M3}$ and $TC°_{Ex}$) frying process. The average temperature of the oil ($TC°_{av}$) was also calculated as the average of all the values recorded in the five zones at the same time.

2.2 Frying experiments

A specific design of experiment (DoE) was defined, based on 65 independent frying experiments for the calibration set and 33 independent frying experiments for the validation set. Independent variables considered in the DoE were: *i*) frying temperature (ranging from 150 °C to 175 °C; n = 5 levels), *ii*) time of frying (ranging from 150 to 180 seconds, n= 5 levels) and *iii*) oil quality (ranging from 100% fresh oil to 100% exhaust oil defined as used oil with a level of total polar material above 12%, n= 5 levels).

For all the frying experiments the same protocol was followed, which included: *i*) washing of the fresh potatoes with cold water and peeling (potato peeler M5, Sammic S.L., Azkoita - Spain) *ii*) immersion of peeled potatoes in cold-water, *iii*) slicing (Robot Coupe CL50 with a 1 mm disk, Dijon, France), and i*v*) final washing with cold water (5 °C).

Oil temperature and time of frying were precisely adjusted to the DoE by the controller of the continuous fryer. The frying tank was filled with 100 L of sunflower oil and oil quality was modified by mixing fresh with exhaust sunflower oil in established proportions according to the DoE. When oil reached the target temperature, a batch of about 4 kg sliced potatoes was loaded in the fryer.

2.4 Process monitoring and sampling

For each one of the 98 independents frying experiments (Calibration and Validation sets), nine CQAs of the raw material and nineteen CQAs (related to oil quality), were monitored during the frying process in addition to three critical process parameters (CPPs). Every day, before starting the frying experiments, ten potatoes were randomly selected from the potato batch, in order to assess the CQAs of the raw material before frying. Each sampled potato was cut in two halves; the first one was used to immediately measure the colour, the second one was divided in five aliquots, which were separately packed in multilayer PP-aluminium bags and immediately stored at -80 ºC.

Oil samples were taken during each frying process with a stainless spoon; samples were immediately transferred in a 100 mL aluminium bottle (ISO Al 99.5; Bürkle, Bad Bellingen, Germany), refrigerated with liquid nitrogen and stored at -80 ºC for chemical analyses.

After processing, and taking out the first kg of sliced potatoes to stabilize the fryer, an aliquot of chips was taken for each one of the frying experiments, then packaged in multilayer PP-aluminium bags and immediately stored at -80 ºC for analysis of twelve QTPs (Quality target Parameters), including both chemical and sensorial parameters related with quality and safety. Average, standard deviation, maximum and minimum of all parameters (CQAs and CPPs) for calibration and validation sets are presented in table 1, while QTPs are presented in table 2.

2.4.1 Colour measurement

Instrumental colour parameters in fresh potatoes samples, before frying, were measured with a Konica Minolta chromameter Model CR-400 HS (Minolta, Tokyo, Japan) with an aperture of 8 mm. In potatoes chips, after frying, a Konica Minolta chromameter Model CR-410 HS (Minolta, Tokyo, Japan) with an aperture of 50 mm was used. In both cases, the equipment was set up for illuminate D65 (2º observer angle) and calibrated using a standard white reflector plate. On the Model CR-400 HS, 5 points were measured for each samples while for the Model CR-410 HS, 3 measurements were taken in succession on a batch of chips. Readings were obtained applying the standard CIE 1976 L^*, a^* and b^* (1976) colour system space.

2.4.2 Total Soluble Solids Content

Total Soluble Solids (TSS) content in fresh potatoes was determined by using a Quick Brix TM90 (Mettler Toledo GmbH, Giessen, Germany). Potatoes samples were smashed, and one drop placed on the refractometer glass, measurements were done in triplicate.

2.4.3 Sugars Content

Sucrose, Glucose and Fructose content in fresh potatoes were quantified by HPLC-RI following the method of Folgado et al., (2014). Briefly, fresh potato samples (4 grams) were homogenised and extracted two times with cold (-20 ºC) ethanol 95%. After centrifugation, an aliquot of the ethanolic fractions was evaporated with N_2, re-dissolved in 0.5 mL of ultrapure water, membrane filtered (pore size 0.2 μm) and injected in the HPLC system (20 μL). Chromatographic separation was carried out with a binary pump 515 equipped with a 2414 Refractive Index detector (Waters, Milford MA, USA) and an Aminex HPX-87C 300 x 7.8 mm column (Bio-Rad, CA, USA) thermostated at 80 ºC. Isocratic elution was carried out with ultrapure MilliQ® water (Merck KGaA, Darmstadt, Germany) at a flow of 0.6 mL/min., and quantification was made with an external calibration curve.

2.4.4 Oil oxidation parameters

Total Polar Material (TPM) in oil was quantified during frying with a cooking oil tester mod. 270 (Testo, Lenzkirch, Germany). Results were express in percentage (%) of Total Polar Material. Data was collected in triplicate during each frying process. Peroxide Index, Acidity Index and p-anisidine value in frying oil were assessed with a FoodLab Fat system (CDR s.r.l, Florence – Italy) following the protocols and the reactants provided by the fabricant.

2.4.5. Fatty acids profile

Fatty acids profile in frying oil was analysed according to Mach et al. (2006). Fatty acid methyl esters (FAMEs) were obtained by following the ISO method 5509E (ISO 5509E, 1978) and analysed using an HP 5890 Series II gas chromatograph (Hewlett Packard SA, Barcelona, Spain). Individual fatty acids (FA) were identified by comparison of their retention times with those of pure standards. Quantification was made by using an internal standard calibration with glyceryl tritridecanoate.

2.4.6. Volatile compounds

Furan, acrolein, hexanal, pentylfuran and 2,4-decadienal in sunflower oils and chips were analysed by SPME-GC/MS with a 6850 Network GC system equipped with a 5975C VL MS axis detector (Agilent Technologies, Santa Clara, CA, U.S.A.) and a Combi Pal autosampler (CTC Analytics AG, Zwingen, Switzerland). One gram of sample was added with 1 µL of mixed internal standard solution (acrolein-^{13}C and hexanal-d_{12}, both at 100 mg/L in isopropanol) in a 10 mL glass vial, vortexed for 30 seconds and pre-incubated at 50 ºC for 2 min at a speed of 500 rpm. A SPME DVB/CAR/PDMS fibre assembly (Supelco, Bellefonte - USA) was used with an extraction time of 30 min and constant agitation at 40 ºC. The chromatographic separation was carried out on a DB-5MS column (30 m, 0.250 mm ID, 1.00 µm film thickness; Agilent J&W GC Columns, Santa Clara CA, USA) with helium as carrier gas at a flow of 0.8 mL/min. Initial temperature of the oven was set at 33 ºC, then followed by a 2 ºC/min ramp up to 50 ºC, a 3 ºC/min ramp up to 72 ºC, a 6 ºC/min ramp up to 180 ºC and a 10 ºC/min ramp up to 220 ºC. For quantification purposes, aliquots of samples were spiked with defined amounts of labelled (acrolein-^{13}C and hexanal-d_{12}) and unlabelled compounds in different mass ratios. The ratios of the area counts for the specific ions of the analytes and the labelled standards were plotted against the ratio of the corresponding concentrations, and the response factors were calculated according to Ewert et al. (2011).

2.4.7 Acrylamide assessment

Acrylamide was quantified in frying oil and chips by HPLC-MS. One gram of frying oil or potato chips were extracted following the protocol of Al-Taher (2012) based on Quechers. Ten μL of the purified extracts were injected in the Agilent 1200 Series HPLC system, equipped with an Agilent 6100 Series Single Quadrupole MS detector (Agilent Technologies, Inc., CA, USA) and a reverse phase C_{18} column (2.1 i.d. x 100 mm, 3 μm). Elution was carried out isocratically with mobile phase A (water: methanol:formic acid 97.4:2.5:0.1) at a flow rate of 0.2 mL/min. MS detector was operated in positive electrospray ionization mode, and the ion with m/z = 72, corresponding to the $[M\text{-}H]^+$ of the acrylamide, was monitored. Quantification was made considering the response of the ion with m/z = 75, corresponding to the molecular ion of the internal standard (acrylamide 13^{C}-3).

2.4.8 Quantitative Descriptive Analyses

Five Sensory descriptors ("odour roast", "flavour rancid", "flavour roast", "crunchy" and "oil mouth feel") were generated by open discussion in two preliminary sessions by eight trained assessors. A non-structured scoring scale was used, where 0 meant the absence of the descriptor and 10 meant the highest intensity of the descriptor. Sensory evaluation was performed for each session time in two sessions (per sampling time) using chips samples corresponding to a frying experiment. Samples were coded using three random numbers and presented to assessors. The first order and the carry-over effects were balanced according to MacFie et al., (1989). For each frying experiment, the average score of the assessors and sessions have been calculated.

2.5. Modelling, Statistics and Aggregation

2.5.1 Multilinear regression and statistic values

Multilinear regression (MLR) coupled to a Step-Wise model (probability for entry: 0.1 and probability for removal: 0.1) was used to develop calibration models on the QTP values from 65 experiments. Two parameters, coefficient of determination of calibration (R^2_{cal}) and probability (Pr > |t|) for each explanatory variables (CQAs and CPPs) were reported. Models were determined using the XLSTAT Premium software version 2018.1 (Addinsoft, France).

The different model gives also a predictive equation and a root mean square error of calibration (RMSEC).

$$\mathrm{RMSEC} = \sqrt{\frac{1}{\mathrm{M}-1} \times \sum_{\mathrm{i}=1}^{\mathrm{M}} \left(\mathrm{y}_{\mathrm{i}}^{\mathrm{ref}} - \mathrm{y}_{\mathrm{i}}\right)^2} \qquad \text{EQ.01}$$

Where:

M is the number of samples

$\mathrm{y}_{\mathrm{i}}^{\mathrm{ref}}$ is the reference value for sample i

y_{i} is the predicted value for sample i

The different models were tested on a validation set of 33 experiments and the quality of the models on each QTP values was assessed with the root mean square error of prediction (RMSEP), coefficient of determination (R^2_{val}), Bias and range error ratio (RER):

$$\mathrm{RMSEP} = \sqrt{\frac{1}{\mathrm{M}} \times \sum_{\mathrm{i}=1}^{\mathrm{M}} \left(\mathrm{y}_{\mathrm{i}}^{\mathrm{ref}} - \mathrm{y}_{\mathrm{i}}\right)^2} \qquad \text{EQ.02}$$

$$\mathrm{Bias} = \frac{\sum_{\mathrm{i}=1}^{\mathrm{M}} (\mathrm{y}_{\mathrm{i}}^{\mathrm{ref}} - \mathrm{y}_{\mathrm{i}})}{M} \qquad \text{EQ.03}$$

$$\mathrm{RER} = \frac{\mathrm{y}_{\mathrm{max}}^{\mathrm{ref}} - \mathrm{y}_{\mathrm{min}}^{\mathrm{ref}}}{\mathrm{RMSEP}} \qquad \text{EQ.04}$$

Where:

y^{ref}_{max} and y^{ref}_{min} are respectively the maximum and minimum values of the validation set

2.5.2 Data aggregation

The idea to aggregate QTPs parameters is to have only one data to describe the quality of our potatoes chips product using a mid-level fusion approach (Borràs et al. 2015). To do so a min-max normalisation of selected quality target product profile was done using equation EQ. 05 followed by the weighting of normalised data (y_i^{norm}) before calculation of the aggregated data (CDF_i) with EQ. 06.

$$y_i^{norm} = \frac{(y_i - y_{min})}{(y_{max} - y_{min})} \qquad \text{EQ.05}$$

$$CDF_i = \sum_{i=1}^{MN} \beta_i \times y_i^{norm} \qquad \text{EQ.06}$$

where M N is the number of selected QTPs, β_i is the weight a number between 0 and 1 and have been selected by authors to give more importance to some QTP parameters.

Four "negative" quality attributes, colour parameter a*, sensory descriptor "flavour roast", acrylamide content and volatiles content pentylfuran content, have been selected to be aggregated. Four aggregated indexes CDF_{I1}, CDF_{I2}, CDF_{I3} and CDF_{I4} have been calculated using EQ. 06 and different weights β_i. In the first aggregation $CDF_{I1,}$ all quality attributes had the same weight [0.25, 0.25, 0.25, 0.25]. For the second one $CDF_{I2,}$ the weights of volatile quality attribute have been reduced to 0.1 and the others increase to 0.3 in order to take more into accounts safety attribute and attributes related with consumer perception. For the third CDF_{I3} [0.2, 0.3, 0.4, 0.1] and fourth CDF_{I4} [0.2, 0.2, 0.5, 0.1] aggregation more emphasis was given to safety issues realty with acrylamide content. In the first aggregation index, $CDF_{I1,}$ all quality attributes [a*, roast, acrylamide, pentylfuran] had the same weight [0.25, 0.25, 0.25, 0.25]. For the second index, $CDF_{I2,}$ the weight of pentylfuran content has been reduced to 0.1 and the others increased to 0.3 in order to highlight safety (acrylamide content) and consumer perception. For the third CDF_{I3} [0.2, 0.3, 0.4, 0.1] and fourth CDF_{I4} [0.2, 0.2, 0.5, 0.1] indexes more emphasis was given to safety issues related with acrylamide content. Weights for a*, flavour roast, acrylamide and pentylfuran are [0.25, 0.25, 0.25, 0.25] for CDF_{I1}, [0.3, 0.3, 0.3, 0.1] for CDF_{I1}, [0.2, 0.3, 0.4, 0.1], for CDF_{I3} and [0.2, 0.2, 0.5, 0.1] for CDF_{I4}. A principal component analysis (PCA) has been carried out on the four quality parameters and the first PCA factor was retained as an additional aggregated index (PCA factor 1).

3. Results

Table 1 shows the average, standard deviation, maximum and minimum values for the selected CQAs as well as for CPPs for the calibration and validation sets. Most of the CQAs display important standard deviations indicating substantial variations in the composition of the raw materials and deep frying conditions and, therefore, including in the predictive models sources of variations usually found in the real processes.

3.1. Multilinear analysis on single QTPs parameters

The coefficient of determination from calibration set (R^2_{cal}), the root mean square error of calibration (RMSEC), the standardized regression coefficients and the p-values from the multilinear regressions calculation are presented in table 2. R^2_{cal} gives the strength of a relationship between exploratory variables and QTPs and it is generally admitted (Moore et al. 2013) that a coefficient above 0.7 indicates that the proposed model explains correctly the variation of the QTPs. Colour parameters a* and b*, sensory descriptors “Odour roast” and “Flavour roast” and volatile parameters hexanal and pentylfuran presented coefficients of determination above 0.7. Others QTPs such as sensory descriptor “Flavour rancid”, acrylamide content and 2.4 decadienal content, showed R^2_{cal} between 0.5 and 0.7, indicating that the predictive models do not explain completely their variations. L*, sensory descriptors "crunchy" and "oil mouth feel" had R^2_{cal} below 0.5, indicating that our models do not explain their variation. Table 2 shows that, out of 29 explanatory variables, 2 to 8 have been retained to explain the variation of each QTPs. On the opposite, 7 explanatory variables (Fructose content, reducing sugars content, TPM, p-anisidine value, fatty acid (FA) 18:2 cis-9 trans-12, ∑FA ɯ6, ∑FA trans and monosaturated fatty acids or MUFA) have not been retained by none of the models to explain variation of the QTPs and were discarded.

MLR models describing QTPs a* and b*, retained respectively 4 and 8 exploratory variables related with raw materials, oil quality, volatile, fatty acids, variables related with oil temperature and process time. For sensory descriptors "odour roast" and "flavour roast", 5 and 4 explanatory variable were respectively retained, related with Sucrose content, L*, hexanal content, saturated FA, oil temperature $TC°_E$ and time. For acrylamide content, the MLR model retained 4 explanatory variables related with red colour, volatile, ratio ɯ6/ɯ3 and $TC°_E$ oil temperature. For QTPs volatiles pentylfuran and 2.4 decadienal, MLR model did not retain any explanatory variable of raw materials, but it retained oil quality parameters, volatile parameter, Saturated FA and $TC°_E$ oil temperature for the first. For QTP 2.4 decadienal only 4 explanatory variables related with oil quality, volatiles and fatty acids. For QTP hexanal, 3 explanatory variables are related with raw materials and 4 with oil characteristics (volatile and fatty acids).

In 5 of the 6 QTPs with a R^2_{cal} above superior to 0.7, exploratory variables related with CPPs have a positive standardized regression coefficients indicating that an increase of temperature or time will increase the different QTPs. Only sensory descriptor "flavour rancid" presents a negative standardized regression coefficient for the exploratory variables $TC°_{av}$. Considering raw materials and oil exploratory variables, positive and negative standardized regression coefficients have been calculated by the model for QTPs a*, b*, "odour Roast", "flavour rancid" and "flavour roast". For volatiles, all QTPs present positive standardized regression coefficients indicating that an increase of all exploratory variables will lead to an increase of the volatiles in the chips. For acrylamide content, an increase of exploratory variable a* will lead to an increase of acrylamide content while an increase of hexanal and ratio ɯ6/ɯ3 will have the opposite effect.

3.2 Prediction with multilinear models

Multilinear model have been used to predict the evolution of selected QTPs with a validation set of 33 experiments. Quality parameters of the prediction are reported in table 3. Taking into account colour parameters of the potatoes chips, only a* presents a coefficient of determination of validation (R^2_{val}) superior to 0.7. For colour parameter b*, results are disappointing with R^2_{val} below 0.5. Models for the sensory descriptors "odour roast" and "flavour rancid" have a R^2_{val} between 0.6 and 0.7, and "flavour roast" has a R^2_{val} above 0.7. For the acrylamide content, when 2 outliers are removed from the analysis, R^2_{val} are between 0.5 and 0.7. Concerning the volatile parameter hexanal, the step-wise model give a R^2_{val} below 0.5, while for volatile parameters pentylfuran and 2-4 decadienal, R^2_{val} are between 0.5 and 0.7.

To summarise, only 2 QTPs (a* and "flavour roast") have a R^2_{val} above 0.7, while others 5 ("odour roast", acrylamide content; hexanal, pentylfuran and 2.4-decadienal) have a R^2_{val} between 0.5 and 0.7. The quality of the models could also be provided by the RER parameters. The QTP acrylamide gives a value of RER of 5.0, while our best predictive models were obtained for sensory descriptors "flavour rancid" and "odour roast" with a respective RER of 6.9 and 6.6. The best RER values ranged between 4.0 and 10.0 indicating that our models have a performance corresponding to screening target (AACC Method 39-00.01).

3.3 Aggregation of QTPs parameters

The contribution of each QTPs to the first PCA factor was 37.2% for a*, 27.8% for “flavour roast”, 27.4% for acrylamide content and 7.6% for pentylfuran. Multilinear regression analyses were conducted on different aggregated indexes and results on the calibration set are shown in Table 4. R^2_{cal} is above superior to 0.7 for 3 of the 4 indexes, CDF_{I4} being the exception with a value of 0.692, and for the first PCA factor, thus indicating that our models can explain the variation of aggregated chips quality parameters. It can be noted that, an increase of the weight of acrylamide content in aggregated indexes, had the effect to reduce R^2_{cal}. Number of explanatory variables retained by the MLR model have been reduced to 7: a* in CDF_{I2}, CDF_{I3} and CDF_{I4}; b* in only one case (CDF_{I1}), when all selected QTPs have the same weight; glucose content in only one case (CDF_{I4}), when the weight of acrylamide content has been set up at 0.5; hexanal volatile content of the oil in CDF_{I2}, CDF_{I3} and CDF_{I4}; ɯ6 content of the oil in only one case (CDF_{I1}); MUFA in CDF_{I2} and CDF_{I3}; Oil temperature $TC°_E$ in all aggregated index. It is significant that all oil quality parameters (TPM, acidity, p-anisidine and peroxide value) have been discarded by the model as well as Time. All standardized regression coefficients of oil temperature $TC°_E$ are positive as well as MUFA and a* and glucose when they are retained by the model. On the contrary, b*, hexanal and ɯ6 present a negative standardized regression coefficients when they are retained.

Models have been applied to the validation data set to explain the variation of our aggregated indexes (table 5). Predictive results of the variation of CDF_{I1}, CDF_{I2} and CDF_{I3} are encouraging with R^2_{val} between 0.668 and 0.728. RER values are between 6.2 and 7.8, indicating a performance target corresponding to screening target. Although first PCA factor shows the best coefficient of determination of validation R^2_{val} with one outlier, the aggregated index CDF_{I2} explained by the Step-Wise model seems to be a good option (Figure 2). Model for the aggregated index CDF_{I2} used only 4 explanatory variables (colour a*, hexanal content, MUFA and oil temperature $TC°_E$), had a R^2_{val} of 0.718 and no outliers in the validation set.

4. Discussion

In order to define the final chips product a total of 12 QTPs, including 3 colour parameters, 5 sensory attributes, 3 volatiles parameters and acrylamide content, have been used. Usually, research works evaluate the impact of some processing parameters on single compounds, like the acrylamide content (Zhang et al. 2015) or texture and oil intake in the potatoes (Pedeschi et al. 2005) but few had a more global approach (Yang et al 2016; Santos et al. 2018).

In the present study only results from MLR algorithm are presented even if non-linear algorithms (Random forest regression and log-linear regression models) have been tested on our dataset. Results of non-linear algorithms have proven to be disappointing. The limited number of independent experiments seems to be a limiting factor to use such non-linear approaches.

Our results show that colour parameters L* and a* had a significant variation that can be explained by CPPs parameters such as the average oil temperature. Yang et al. (2016) had have compared the evolution of colour of potatoes strips retrieved issue from Agria, Kennebec and Red Pontiac cultivars regarding oil temperatures and frying time 190°C / 160 s, 170°C / 240 s, 150°C / 330 s. In contrast with our results, few colour variations of the final products have been measured for Agria cultivar, much more have been detected for the other two cultivars. Pedreschi et al. (2005) proved that the oil temperature and time of frying is related to the colour a* parameter of the potato and the acrylamide formation. Our predictive results for acrylamide are lower than expected but some positive points could be extracted. Yang et al. (2016) established that the correlations between selected studied factors of raw materials (such as asparagine, fructose, glucose, sucrose, reducing sugar, oil uptake, colour L*, colour b* and shear force) were significant to explain the acrylamide content in the final product. Some of the parameters have been measured in our study and the explanatory variables colour a*, hexanal content, ratio ω6/ω3 and average frying temperature have been used by the MLR model to explain and predict the variation of acrylamide content. Our study, as a new approach, took into account sensory attributes, because chip taste is related with Maillard reactions, which is the main responsible for the formation of acrylamide (Lee & Shibamoto, 2002). However, no clear relationship (R^2<0.5) could be found between measured acrylamide content and sensory descriptors or other compositional parameters of potatoes chips. Even if such results are in discrepancy with finding of Pedreschi et al. (2005), it should be pointed out that a different cultivar was used (Agria versus Panda) and that our experiment was carried out with a continuous semi-industrial fryer and using oil at different degree of oxidation to mimic the industrial condition. On the other hand, formation of acrylamide involves complex mechanism reactions that probably the CQAs and CPPs included in the model cannot describe completely (Purlis, 2010).

Aggregated indexes with different QTPs parameters describing potatoes chips characteristics have also been analysed, in order to predict a global potatoes chips quality. In food science, low and mid-level data fusion have been undertaken for a wide range of applications such as quality parameters correlation, sensory properties assessment, cultivar selection or origin authentication (Borras et al., 2015). In our case, four parameters describing potatoes chips have been used, and different weight has been given to acrylamide content. Using aggregated data indexes a compromise have been found between the need to obtain safe products with lower acrylamide contents, but taking into accounts the sensory profile. Whatever the aggregated index selected to obtain the "best product", within the experimental domain here studied and with our frying equipment, we should use fresh potatoes with highest intensity of yellow/green colour (highest b* and lowest a* values) and the lowest frying oil temperature (150 ºC). As time did not appear as an explanatory variable in aggregated indexes, we could use the shortest time (150 seconds) to achieve the maximum production efficiency. If we consider CDF_{I4}, which gives more importance to acrylamide content, fresh potatoes with the lowest glucose content should be selected. MUFA, hexanal and ω6 oil contents are indicators of the oil quality. The variation of these parameters with respect to those of the fresh oil could be used to establish the oil turnover, which will depend on the aggregated index selected.

In the present work, online measurements were possible for some of the attributes, such as colour parameters (L*, a* and b*) in raw materials, oil quality (TPM) and process parameters (time and temperature), but others key parameters (sugar content of raw materials, volatiles, fatty acids) were analysed off-line at laboratory scale. So, future improvements of Quality by Design approach are also strictly linked to the implementation of suitable online analytical methods for a comprehensive monitoring of the process.

5. Conclusion

The Quality by Design approach has been used to identify the main quality and process parameters that can be modified for the production of deep-fried potatoes "chips". To conduct processing, specific target parameters related with sensory descriptors could be predicted with MLR models with some accuracy by measurement of few explanatory variables related with potatoes brightness, oil volatile, saturated fatty acid and oil temperature, but for safety issues such as acrylamide content the predictive models are far from satisfactory. A general aggregated index incorporating 4 different quality parameters of the chips can be predicted with a reasonable accuracy, and can be used to establish the optimal process conditions. They are still a number of complex mechanisms and factors to be identified that can influence the quality parameters of potatoes chips. The work had shown the need of further studies to explore the data fusion strategies for quality parameters of the final products to define single parameter that can be easily predicted and still full fit the goal to optimise sustainable processing.

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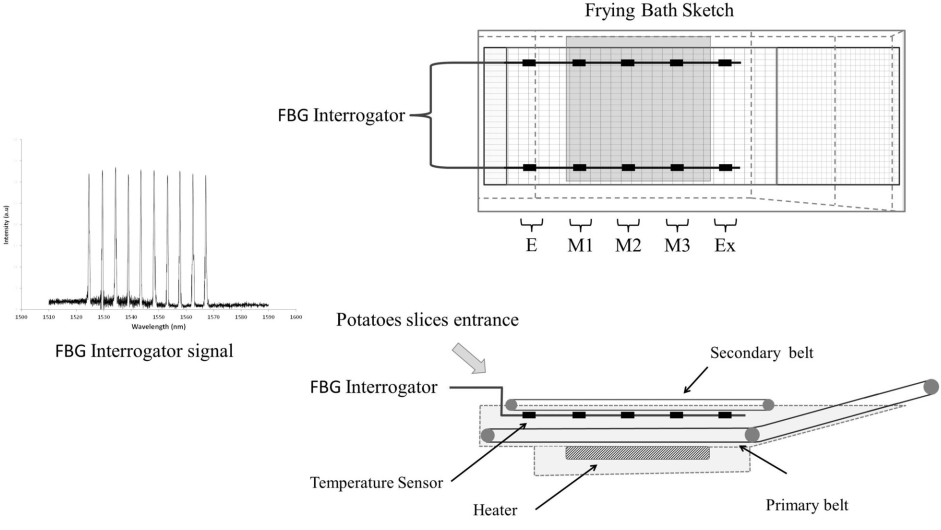
Frying Bath Sketch
FBG Interrogator
E
M1
M2
M3
Ex
Intensity (a.u)
1500
1510
1520
1530
1540
1550
1560
1570
1580
1590
1600
Wavelength (nm)
FBG Interrogator signal
Potatoes slices entrance
Secondary belt
FBG Interrogator
Temperature Sensor
Heater
Primary belt

Figure 1

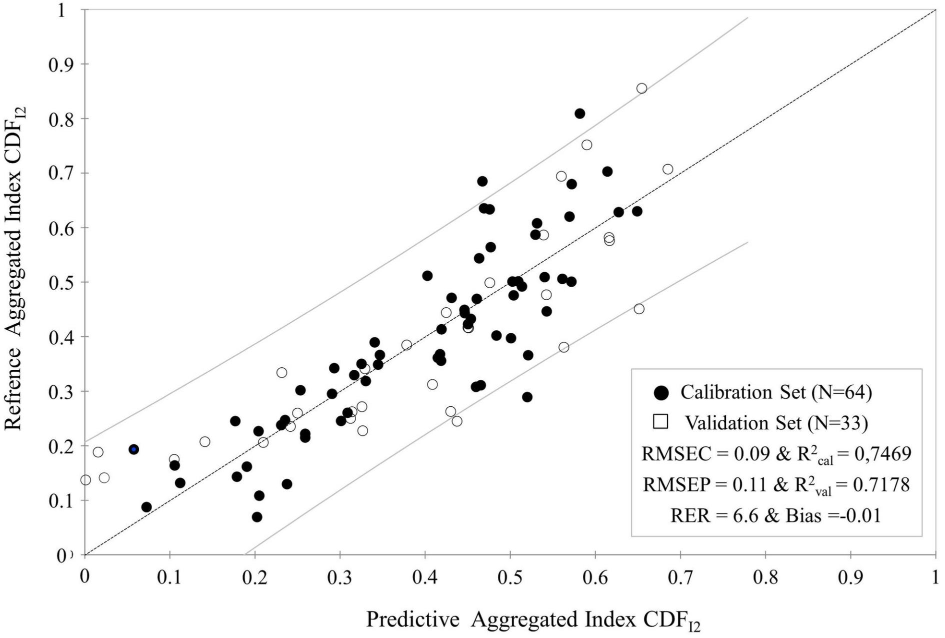
Refrence Aggregated Index CDF$_{I2}$
Predictive Aggregated Index CDF$_{I2}$
Calibration Set (N=64)
Validation Set (N=33)
RMSEC = 0.09 & R^2_{cal} = 0,7469
RMSEP = 0.11 & R^2_{val} = 0.7178
RER = 6.6 & Bias =-0.01

Figure 2

Table 1: Mean ±standard deviation (SD), maximum and minimum of the different critical quality attributes (CQAs) and Quality Process Parameters (CPPs) measured for the calibration set (N=65) and Validation Set (N=33). TPM stands for total polar materials; FA stands for fatty acid; MUFA stands for monosaturated fatty acids; PUFA stands for polysaturated fatty acids.

		Calibration Set (N = 65)			Validation Set (N=33)		
		Mean	Max	Min	Mean	Max	Min
Potatoes CQAs	L*(CIELAB)	66.4 ±1.1	68.5	62.7	66.4 ±1.6	68.5	62.7
	a*(CIELAB)	-3.6 ±0.8	-2.7	-5.6	-3.6 ±0.9	-2.7	-5.6
	b*(CIELAB)	14.4 ±5.0	25.1	10.2	14.4 ±5.4	25.1	10.2
	TSS (°Brix)	1.8 ±0.3	2.5	1.2	1.8 ±0.4	2.5	1.2
	Sucrose (mg/100L)	575 ±157	759	217	633 ±124	759	217
	Glucose (mg/100 L)	215 ±128	500	26	236 ±146	500	26
	Fructose (mg/100 L)	299 ±60	447	198	319 ±64	447	198
Oil CQAs	TPM (%)	8.6 ±3.6	15.1	1.1	8.3 ±3.6	14.3	1.7
	Acidity index (%)	0.30 ±0.22	0.81	0.03	0.26 ±0.19	0.73	0..04
	p-anisidine value	14.2 ±15.3	46.9	0.5	13.3 ±15.7	48.6	0.5
	Peroxide index (meqO2/kg)	4.8 ±2.8	14.5	1.0	4.2 ±2.2	10.4	1.2
	Acrolein (ppb)	499 ±245	1205	150	548 ±237	1017	155
	Furan (ppb)	38 ±28	139	1	35 ±25	133	4
	Hexanal (ppm)	2.15 ±0.77	5.21	0.59	2.26 ±0.78	4.40	1.24
	Pentylfuran (ppm)	1.71 ±0.68	3.69	0.12	1.76 ±0.81	5.10	0.51
	2,4-decadienal (ppm)	137 ±96	445	0	158 ±115	553	23
	FA 18:1 trans ɯ9 (%)	0.13 ±0.08	0.28	0	0.11±0.07	0.27	0.00
	FA 18:2 cis-9 trans-12 (%)	0.07 ±0.02	0.16	0.04	0.07±0.01	0.09	0.02
	FA 18:2 trans-9 cis-12 (%)	0.07 ±0.01	0.11	0.05	0.07±0.01	0.10	0.04
	∑FA ɯ6 (%)	8.4 ±1.1	10.0	6.5	8.5 ±1.0	9.8	6.5
	∑FA trans (%)	0.27 ±0.07	0.41	0.13	0.25 ±0.07	0.38	0.14
	Ratio ɯ6/ ɯ3	152 ±64	414	40	147 ±56	229	26
	∑FA ɯ3 (%)	0.06 ±0.03	0.24	0.02	0.07 ±0.05	0.32	0.04
	Saturated FA (%)	9.3 ±0.2	9.8	8.9	9.3 ±0.3	9.8	8.8
	MUFA (%)	82 ±1	84	80	82 ±1	84	80
	PUFA (%)	8.4±1.1	10.0	6.5	8.5 ±1.0	9.9	6.6
CPPs	Time (s)	164 ±10	180	150	164 ±10	180	150
	$TC°_{av}$ (°C)	159 ±7	172	147	158 ±8	172	147
	$TC°_{E}$ (°C)	157 ±7	170	142	156 ±8	169	144

Table 2: Standardized regression coefficients and p-value (Pr > |t|) in parenthesis of the F statistic from an analysis of variance (ANOVA) and coefficient of determination R^2_{cal} , Root Mean Square Error of calibration (RMSEC) of the multi linear regression (MLR) using the model Step-wise (probability for entry: 0.1 and probability for removal: 0.1) for the different QTPs of potatoes chips. FA 18:2 trans(2) stands for FA 18:2 trans-9 cis-12; FA stands for fatty acid; PUFA stands or polysaturated fatty acids.

	Quality Target Parameters (QTPs) of potatoes chips											
	Colour			Sensory					Safety	Volatiles		
	$L^*_{(CIELAB)}$	$a^*_{(CIELAB)}$	$b^*_{(CIELAB)}$	Odour Roast	Flavour rancid	Flavour Roast	Crunchy	Oil Mouth feel	Acrylamide	Hexanal	Pentylfuran	2.4decadienal
R^2_{Cal}	0.375	0.711	0.739	0.777	0.633	0.764	0.439	0.480	0.539	0.729	0.755	0.642
RMSEC	3.6	1.4	1.7	0.7	0.7	0.8	0.5	0.6	0.68 ppm	99 ppb	82 ppb	10 ppm
$L^*_{(CIELAB)}$						0.12 (0.066)		0.33 (0.004)		0.26 (0.004)		
$a^*_{(CIELAB)}$									0.46 (<0.001)			
$b^*_{(CIELAB)}$		-0.20 (0.037)	0.51 (< 0.001)									
TSS			-0.17 (0.020)					-0,23 (0.031)		-0.22 (0.010)		
Sucrose				-0.17 (0.056)	-0.16 (0.070)					-0.35 (<0.001)		
Glucose		0.39 (< 0.001)			0.39 (<0.001)							
Acidity			-0.49 (<0.001)				-0.45 (< 0.001)	-0.28 (0.095)			0.36 (0.006)	
peroxide											0.16 (0.089)	0.21 (0.018)
Acrolein			-0.17 (0.042)					-0.22 (0.034)				
Furan				-0.32 (0.002)	-0.30 (0.024)	-0,14 (0.039)	0.18 (0.093)					
Hexanal	0.41 (<0.001)	-0.19 (0.017)					0.26 (0.009)		-0.35 (<0.001)	0.20 (0.028)		0.37 (< 0.001)
Pentylfuran					0.36 (0.007)					0.43 (< 0.001)	0.47 (< 0.001)	
2.4-decadienal										-0.21 (0.013)		0.30 (0.001)
FA 18:1 trans ɯ9				0.21 (0.043)				-0.36 (0.320)				
FA 18:2 trans(2)										0.33 (<0.001)		
∑FA trans												
Ratio ɯ6/ ɯ3									-0.21 (0.063)			0.30 (0.001)
∑FA ɯ3			0.17 (0.025)		-0.20 (0.037)							
Saturated FA						-0,16 (0.020)					0.33 (< 0.001)	
PUFA			-0.34 (0.015)									
Time (s)			0.14 (0.063)	0.13 (0.083)	0.20 (0.027)							
$TC°_{av}$ (°C)			0.40 (< 0.001)		-0.44 (< 0.0001)		0.42 (< 0.0001)					
$TC°_{E}$ (°C)	-0.48 (< 0.001)	0.79 (< 0.001)		0.77 (< 0.001)		0.83 (< 0.001)			0.54 (< 0.001)		0.23 (0.002)	

Table 3: Validation of the different models used to explain the variability of selected QTPs. N_v: number of experiments from the validation set; R^2_{Val}: coefficient of determination of the validation set; RMSEP: root mean square error of prediction; Bias: model bias; RER: range error ratio.

QTPs	N_v	R^2_{Val}	RMSEP	Bias	RER
$a^*_{(CIELAB)}$	33	**0.789**	1.6	0.0	5.1
$b^*_{(CIELAB)}$	31	0.316	2.5	-0.4	4.8
Odour Roast	32	0.656	0.8	0.0	6.4
Flavour Rancid	33	0.614	0.7	0.0	6.9
Flavour Roast	33	**0.736**	0.9	0.0	6.6
Acrylamide (ppm)	31	0.520	0.9	0.0	5.0
Hexanal (ppb)	32	0.319	137	13	4.1
Pentylfuran (ppb)	32	0.613	91	25	5.7
2.4decadienal (ppm)	32	0.514	10	1.4	5.5

Table 4: Standardized regression coefficients and p-value (Pr > |t|) in parenthesis of the F statistic from an analysis of variance (ANOVA) and coefficient of determination R^2_{cal} , Root Mean Square Error of calibration (RMSEC) of the multi linear regression (MLR) using the model Step-wise (probability for entry: 0.1 and probability for removal: 0.1) for PCA factor 1 and aggregated indexes CDF_{I1}, CDF_{I2}, CDF_{I3} and CDF_{I4}. MUFA stands for monosaturated fatty acids

	CDF_{I1}	CDF_{I2}	CDF_{I3}	CDF_{I4}
R^2_{Cal}	0.778	0.747	0.719	0.692
RMSEC	0.08	0.09	0.09	0.10
$a^*_{(CIELAB)}$		0.29 (<0.001)	0.33 (<0.001)	0.39 (< 0.001)
$b^*_{(CIELAB)}$	-0.27 (0.001)			
Glucose				0.23 (0.010)
Hexanal		-0.16 (0.028)	-0.19 (0.015)	-0.25 (0.002)
∑FA ɯ6	-0.37 (< 0.001)			
MUFA		0.24 (0.003)	0.21 (0.010)	
$TC°_E$	0.81 (< 0.001)	0.84 (< 0.001)	0.82 (< 0.001)	0.81 (< 0.001)

Table 5: Validation of the different models used to explain the variability of PCA factor 1 and aggregated indexes (CDF_{I1}, CDF_{I2}, CDF_{I3} and CDF_{I4}). N_v: number of experiments from the validation set; R^2_{Val}: coefficient of determination of the validation set; RMSEP: root mean square error of prediction; Bias: model bias; RER: range error ratio.

	N_v	R^2_{Val}	RMSEP	Bias	RER
PCA factor 1	32	**0.747**	0.84	-0.07	7.1
CDF_{I1}	32	**0.728**	0.09	0.00	6.9
CDF_{I2}	33	**0.718**	0.11	-0.01	6.6
CDF_{I3}	33	0.668	0.12	0.00	6.2
CDF_{I4}	32	0.650	0.14	0.00	5.5