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Unravelling effects of flavanols and their derivatives on acrylamide formation *via* support vector machine modelling

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ABSTRACT

This study investigated the effect of flavanols and their derivatives on acrylamide formation under low-moisture conditions *via* prediction using the support vector regression (SVR) approach. Acrylamide was generated in a potato-based equimolar asparagine–reducing sugar model system through oven heating. Both positive and negative effects were observed when the flavonoid treatment ranged 1–10,000 μmol/L. Flavanols and derivatives (100 μmol/L) suppress the acrylamide formation within a range of 59.9–78.2%, while their maximal promotion effects ranged from 2.15-fold to 2.84-fold for the control at a concentration of 10,000 μmol/L. The correlations between inhibition rates and changes in Trolox-equivalent antioxidant capacity (ΔTEAC) ($R_{TEAC\text{-}DPPH}$ = 0.878, $R_{TEAC\text{-}ABTS}$ = 0.882, $R_{TEAC\text{-}FRAP}$ = 0.871) were better than promotion rates ($R_{TEAC\text{-}DPPH}$ = 0.815, $R_{TEAC\text{-}ABTS}$ = 0.749, $R_{TEAC\text{-}FRAP}$ = 0.841). Using ΔTEAC as variables, an optimized SVR model could robustly serve as a new predictive tool for estimating the effect (*R*: 0.783–0.880), the fitting performance of which was slightly better than that of multiple linear regression model (*R*: 0.754–0.880).

1. Introduction

Acrylamide, a chemical contaminant of wide concern discovered during thermal processing, has been classified as a probable carcinogen to humans (Group 2A substance) by the International Agency for Research on Cancer (IARC, 1994). The neural, genetic and reproductive toxicities of acrylamide have also been widely acknowledged. Numerous laboratories and institutes have participated in ongoing investigations regarding the formation and reduction of acrylamide (Pedreschi, Mariotti, & Granby, 2014; Xu et al., 2014). Acrylamide is generated from Maillard reaction between the amino acid asparagine and carbonyl compounds (Mottram, Wedzicha, & Dodson, 2002; Stadler et al., 2002). Several pathways (e.g., asparagine and acrolein pathways) and key intermediates (e.g., Schiff base, Amadori products and 3-aminopropionamide) have been proposed as contributing to the formation of acrylamide (Vinci, Mestdagh, & De Meulenaer, 2012).

The production of acrylamide in foods submitted to heat processing such as frying, baking and roasting, needs a low-moisture medium. Water activity in food matrices could affect the reaction rates of lipid oxidation, browning, enzyme activity and microbial growth, implying an interaction between the chemical reactivity and physical changes during acrylamide formation. The Schiff base, a condensate of reducing sugar and asparagine, and an intermediate product in the Maillard reaction, facilitates the decarboxylation step and contributes to the generation of the decarboxylated Schiff base *via* the formation of oxazolidin-5-one by intramolecular cyclization (Liu et al., 2015). Knowing that the Schiff base formation is reversible, the elimination of a water molecule from the reducing sugar and asparagine is suggested to be rate-determining at higher water activities, whereas the increase in the energy of activation (and enthalpy of activation) is accordingly counteracted by a more positive entropy of activation, in agreement with the decarboxylation as a rate-determining step at low water activity. That is to say, increasing the initial water activity clearly results in decreasing system reactivity in term of acrylamide formation/elimination (Bassama et al., 2011). The same trend was also reported in real foods, where acrylamide formation was found to occur to a large extent only when the moisture content was below 5% (Elmore, Koutsidis, Dodson, Mottram, & Wedzicha, 2005). A previous study revealed that a lower initial water activity in the reaction system leads to a greater reactivity of the acrylamide formation/elimination, while increasing the

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water content results in an enhancement of the mobility of molecules (Bassama et al., 2011). Therefore, the role of the moisture state on acrylamide generation should be especially taken into consideration. Hence, a fundamental formation study as well as the heat processing parameter optimization of acrylamide should be a prerequisite research. More studies are expected to elucidate the formation mechanism of acrylamide *via* the effect of moisture and pursue the reduction of acrylamide under a low-moisture reaction system.

As acrylamide is a by-product of the Maillard reaction, the major challenge of reduction studies is to constrain acrylamide hazards as much as possible, while maintaining the color, taste, texture and flavour attributes of the foods (Xu et al., 2014). Numerous mitigation strategies have to date been proposed for the control of acrylamide, which mainly include the modification of raw materials and optimization of the heat processing parameters as well as the application of exogenous additives (Zhang, Ren, & Zhang, 2009). Several studies have been carried out to evaluate the chemoprevention effects of herbal extracts on acrylamide reduction (Kahkeshani, Saeidnia, & Abdollahi, 2015). A previous study demonstrated that antioxidant extracts from green tea, cinnamon and oregano effectively reduced the formation of acrylamide by up to 62%, 39% and 17% in fried potatoes, respectively (Morales, Jimenez, Garcia, Mendoza, & Beristain, 2014). The reduction of acrylamide was also achieved in fried chicken drumsticks and chicken wings by the addition of green tea extract (Demirok & Kolsarici, 2014). Flavanols and their derivatives exert their antioxidant properties to reduce acrylamide formation, presumably by trapping carbohydrates and/or preventing lipid oxidation in fat-rich systems (Capuano, Oliviero, Açar, Gökmen, & Fogliano, 2010). Nevertheless, few studies have mechanistically investigated the effect of flavanols and derivatives on the reduction of acrylamide with a view of the structure-activity relationship or kinetics in the low-moisture system.

The dual effect of some food additives on acrylamide formation has also been found in low-moisture reaction systems. For example, the addition of glutamine results in a significant increase in the rates of both acrylamide formation and elimination, while cysteine exerts a pronounced reducing effect (>99%) on the acrylamide yield, indicating that these amino acids may competitively reduce or promote the interaction between asparagine and glucose in model reaction systems under low-moisture conditions (De Vleeschouwer, Van der Plancken, Van Loey, & Hendrickx, 2009a). However the type of sugar, monosaccharide or disaccharide, had only a limited impact on the production of acrylamide (De Vleeschouwer, Van der Plancken, Van Loey, & Hendrickx, 2009b). Several studies have explored the correlation between the addition of natural extracts and the formation/elimination of acrylamide. The addition of the antioxidant of bamboo leaves or extract of green tea could reduce the formation of acrylamide during the formation-predominant kinetic stage and prolong the formation progress of acrylamide in a low-moisture reaction system (Zhang & Zhang, 2008). Moreover, six polyphenols (caffeic acid, chlorogenic acid, ellagic acid, epicatechin, punicalagin and tyrosol) reduced the formation of acrylamide in asparagine–fructose model system but the polyphenol oleuropein exhibited a promotion effect (Oral, Dogan, & Sarioglu, 2014). However, chlorogenic acid added to the asparagine–glucose Maillard reaction system significantly increases acrylamide formation and inhibits its elimination. In contrast, the quinone derivative of chlorogenic acid decreases acrylamide formation (Cai et al., 2014). The results suggest that antioxidant and pro-oxidant behaviours related to acrylamide formation and/or elimination both exist in natural antioxidants. Unfortunately, the available studies for us to understand the mechanism between the reduction of acrylamide and the antioxidant and pro-oxidant properties of the natural antioxidants are limited.

Considering the antioxidant-dependent association, the antioxidant property of Maillard reaction products (MRP) may be used to predict the reduction and promotion of acrylamide. Support vector machines (SVM) are powerful machine learning models with associated learning algorithms that analyse data used for classification and regression analysis (Noble, 2006). The idea of the input vectors, which are non-linearly mapped to a very high-dimension feature space is carried out conceptually (Cortes & Vapnik, 1995). In this feature space a linear decision surface, a hyperplane, is constructed. Given the labelled feature vectors, a hyperplane could separate the positively labelled samples from the negatively labelled samples while ensuring that the closest point in each class is as far away as possible from the hyperplane (Vidyasagar, 2015). As a cutting-edge modelling approach, special properties of the decision surface ensure high generalisation ability of the learning machine, including the use of kernels, the absence of local minima, the sparseness of the solution and the capacity control achieved by optimising the margin (Laanaya, Abdallah, Snoussi, & Richard, 2011). Unfortunately, we have not found any previous predictive work using the support vector regression (SVR) approach yet.

Our previous study showed that the selected flavanols and their derivatives exhibited reduction effects on acrylamide formation during microware heating treatment through antioxidant-related and kinetic studies (Cheng, Chen, Lu, Chen, & Zhang, 2014). In this study, we innovatively used the SVR approach to evaluate the dual effect of flavanols and their derivatives on acrylamide formation in a low-moisture system when using different addition levels of flavonoids via comparison using a general multiple linear regression (MLR) approach, and take a deeper look at the antioxidative characteristic of the natural antioxidants.

2. Materials and methods

2.1. Chemicals and materials

Epicatechin (EC), epicatechin gallate (ECG), epigallocatechin (EGC) and epigallocatechin gallate (EGCG) were supplied by the Tea Research Institute of Chinese Academy of Agricultural Sciences (Hangzhou, China). Acrylamide, L-asparagine monohydrate, D-(+)-glucose monohydrate, 2,2-Diphenyl-1-picrylhydrazyl (DPPH), 2,2-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox), potassium persulfate and 2,4,6-tri(2-pyridyl)-*s*-triazine (TPTZ) were purchased from Sigma-Aldrich (St. Louis, MO, USA). D_3-labelled acrylamide (isotopic purity $\geqslant$ 99%) was obtained from Cambridge Isotope Laboratories (Andover, MA, USA). Potato powder (Atlantis variety) was purchased from Sanjiang (Group) Potato Products Co., Ltd. (Lintao, Gansu, China).

2.2. Preparation of low-moisture Maillard reaction system

The role of flavanols and derivatives in acrylamide formation was investigated using a potato-based equimolar asparagine–reducing sugar Maillard reaction system. The heating of the reaction in a low-moisture system was achieved via routine oven heating. The reactant powders of asparagine (0.14 mol) and glucose (0.14 mol) were mixed with the potato powder (50 g) through careful grinding to ensure enough surface area for the reaction. According to our previous study using high-performance liquid chromatography (HPLC) (Cheng, Chen, Zhao, & Zhang, 2015), the original contents of asparagine (0.037 mg) and glucose (0.015 mg) in potato powder (100 mg) were negligible when compared to the addition levels of asparagine (1 mmol) and glucose (1 mmol) in this experiment.