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Short communication

Modeling in food and bioproducts processing using Boltzmann entropy equation: A viewpoint of future perspectives

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ABSTRACT

This viewpoint discusses the possibility of developing stochastic models in food and bioproducts processes based on the thermodynamic properties of the involved molecules and particularly a generalized approach of Boltzmann entropy equation ($S = k \cdot \ln W$). To this line, enzyme kinetics modeling is discussed as a bioengineering practice to explore relationships between processes, structures and functions in food products, prior describing the macro- and micro-states according to Boltzmann entropy equations. Thereafter, two case studies (starch hydrolysis and β-glucan microstates) that followed this approach are critically revised. Finally, the possibility of applying this concept in modeling efforts of other applications in bioproducts processing, food industry, and food waste recovery are highlighted.

1. Introduction

The new trend in food and bioproducts processing requires the development of safer, tastier, cheaper and tailor-made and sustainable products (Galanakis, 2013, 2016, 2017). To this direction, functional compounds are today used as additives in foodstuff due to their ability to improve the technological properties of the final product and provide health claims, respectively (Ramaa et al., 2006; Galanakis et al., 2013; Granato et al., 2017). For example, macromolecules (e.g. pectin, β-glucan) are known for their ability to lower blood lipid level and show advanced gelling properties that can replace fat in foods, stabilize emulsions and improve product's shelf-life (Rodríguez et al., 2006; Galanakis et al., 2010c; Galanakis, 2011). The recovery of functional compounds is nowadays investigated through undervalued bioresources that are pretreated, prior the separation of macro- and micro-molecules with different procedures (Galanakis, 2012, 2015). Besides, larger and smaller functional molecules exist in clusters inside bioresource matrixes, e.g. phenols bind either dietary fibers of plant materials (Bravo et al., 1994) or dietary proteins (non-covalently) (Rawel et al., 2005). In order to break down these clusters, hydrolytic processes are typically applied using either enzymes or chemical agents. After a certain extent of substrate conversion, hydrolysis results in several derivatives of different concentrations that are difficult to be predicted.

2. Enzyme kinetics modeling

Modeling as a bioengineering practice has found a role in exploring relationships between processes, structures and functions. For instance, enzyme kinetics modeling uses standard compound information to explore pathways and reaction mechanisms of complex macromolecular substrates prior to developing process control strategies to solve the aforemen-

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tioned issues and ensure desired efficacy (McDermott and Klein, 1986; Sin et al., 2009). Enzyme kinetics modeling has been applied in several applications to:

(i) monitor enzymatic hydrolysis of polymers' (e.g. starch, protein and β-glucan) containing substrates and wastes (Kettunen et al. 1996; Del Re et al., 2003; Pinto et al., 2005),
(ii) accelerate depolymerization reactions (McDermott et al., 1990; Carbonel et al., 1998),
(iii) improve fermentation processes conducted by free and immobilized cells (Huang et al., 2002; Galanakis et al., 2012),
(iv) enhance inulinase and delivered fructooligosaccharides production (Mazutti et al., 2010)
(v) control biotransformation procedures leading to pharmaceuticals such as L-carnitine (Hoeks et al., 1996),
(vi) optimize the yield of membrane bioreactors that use immobilized enzymes (e.g. thermolysin or tyrosinase) with a final purpose of removing of peptides or phenols, respectively, from food waste streams (Trusek-Holownia and Noworyta, 2008; Calabrò et al., 2009).

An overview of the different modeling techniques concerning this kind of processes have been revised by Galanakis et al. (2012). According to the applied methodologies, enzyme kinetics and related models can be classified in three major groups: (i) deterministic, (ii) empirical and (iii) stochastic. Most of the cited studies dealt either with fundamental deterministic models or empirical equations directly from multi-factorial experimental designs. Although deterministic models can provide a satisfactory compatibility with experimental data, they basically assume a homogenous substrate structure, predict up to a couple of final products and examine only the end products (Wojciechowski et al., 2001; Galanakis et al., 2012). Calculating of intermediate concentrations has typically been performed using differential equations. This is far more complicated for multiple (enzymatic or substrate) systems (Bryjak et al., 2000) since in practice it is rather impossible to receive a mathematical solution. For instance, some numerical methods may fail to converge to a numerical solution and/or numerical simulations may be longer due to the high degrees of freedom to be solved. On the other hand, if a model is well-posed, the number of equations should not be a deterrent to obtain a mathematical solution.

Empirical models have alternatively been applied (Paolucci-Jeanjean et al., 2000), but they predict only the formation of a limited carbohydrates number. On the other hand, stochastic models can be applied easier instead of analytical methods, since they can simulate the breakdown of all carbohydrates without calculating numerous parameters and estimating multiple dependent equations. Indeed, simulation is performed by converting each reaction in a discrete event and thus the respective probability has to be reflected to a discrete action (Marchal et al., 2003). Among the different stochastic methods, Monte Carlo technique is very popular in the monitoring of degradation procedures, e.g. starch hydrolysis. Particularly, a pseudorandom number mentioning the polymer linkage attacked by an enzyme is generated to predict quantitatively hydrolysis procedure. Moreover, it is assumed that the enzyme can split off substrates from the attacked point on the strength of defined enzyme specification (Wojciechowski et al., 2001).

3. Macro- and micro-states in Boltzmann entropy equations

Any macroscopic system is composed of microscopic parts that contribute to its whole functioning. However, the dynamics of the whole macroscopic system may behave differently compared to the behavior of the component microscopic parts. Matter is composed of molecules, e.g. the macroscopic state of a perfect gas is defined by given values of the pressure (P), volume (V) and temperature (T). On the other hand, this gas could be resulted by a given number of microstates (N) reflecting the different positions and velocities of its billion molecules (Bianciardi and Ulgiati, 2004). Boltzmann (1872) assumed that all the N molecules constituting a gas have the same velocity and size, and divided the volume V into a very large number of cells (M). Then, the number of distinct microstates N corresponding to the macrostate of volume V could be established by:

$$\mathrm{N} = \frac{n_{\mathrm{i}}}{n_1 \ldots . n_{\mathrm{M}}!} \tag{1}$$

where n_{i} is the number of molecules contained in the i-th cell and:

$$n = \sum\nolimits_{\mathrm{i}} n_{\mathrm{i}}. \tag{2}$$

Boltzmann also assumed that the entropy of the state is linked to the number N of microstates by the expression:

$$S = k \cdot \log\ N \tag{3}$$

where S is the entropy and k is Boltzmann constant. Could the latest equation be used to predict reactions of food and by-products processing in a stochastic model?

4. Models based on Boltzmann entropy equations

Instead of employing the classic stochastic tools like Monte Carlo model, Maniatis et al. (2008) proposed to simulate a defined process or system (e.g. starch hydrolysis) according to the thermodynamic properties of the involved molecules. As referred, the concepts of entropy, information and sensation could be expressed by the natural logarithm equivalent notation of Boltzmann equation:

$$S = k \cdot \ln W, \tag{4}$$

where k is the Boltzmann constant (equal to 1.38065×10^{-23} J/K) and W is multiplicity, defined as the number of possible events, arrangements or microstates. An accumulation of multiplicity (W) produces an increased and logarithmically related feeling intensity of the entropy (S). The equation is known as the Shannon equation regarding information, which is called the Hausdorf property symbolized by H. For sensation, the equation is known as the Weber–Heffner Law (Maniatis et al., 2008).

Multiplicity could be estimated by microstates or combinatorial theory that deals with the study of finite discrete structures (Demaine, 2001). In fact, combinatorics count the structures of a given kind and size, deciding the compliance of certain criteria. According to Maniatis et al. (2008), Boltzmann equation could be extended in a generalized man-