Journal of Food Engineering 192 (2017) 61–71

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Dynamic modelling of pectin extraction describing yield and functional characteristics

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ARTICLE INFO

Article history:
Received 26 May 2016
Received in revised form
9 August 2016
Accepted 11 August 2016
Available online 12 August 2016

Keywords:
Pectin extraction
Dynamic modelling
Yield
Degree of esterification
Intrinsic viscosity

ABSTRACT

A dynamic model of pectin extraction is proposed that describes pectin yield, degree of esterification and intrinsic viscosity. The dynamic model is one dimensional in the peel geometry and includes mass transport of pectin by diffusion and reaction kinetics of hydrolysis, degradation and de-esterification. The model takes into account the effects of the process conditions such as temperature and acid concentration on extraction kinetics. It is shown that the model describes pectin bulk solution concentration, degree of esterification and intrinsic viscosity in pilot scale extractions from lime peel at different temperatures (60 °C, 70 °C, 80 °C) and pH (1.5, 2.3, 3.1) values.

1. Introduction

Pectin is a family of complex polysaccharides primarily present in plant cell walls. The three main components of pectin are homogalacturonan (HG), rhamnogalacturonan I (RG-I) and rhamnogalacturonan II (RG-II). From an industrial point of view HG is the most interesting part of pectin and is composed of a chain of α-1,4 linked galacturonic acid residues. Some of the residues may be acetylated or esterified/methoxylated (Willats et al., 2006). Pectin is widely used in many food and pharmaceutical products for modification of rheological properties. The worldwide market for pectin exceeds 45,000 tonnes and represents a value of more than 400 million EUR (Savary et al., 2003). Citrus peel from lemon, orange and lime is the main source of raw material for industrial production of pectin and citrus peel is also a convenient raw material as it is the residual product from juice production. Industrially, pectin is extracted i.e. leached from citrus peels by acid hydrolysis, and subsequently recovered by precipitation with alcohol (Graham and Sheperd, 1953; Minkov et al., 1996).

A pectin factory receives shipments of peels of different citrus fruits from various geographical locations and therefore there is a variation in properties and chemical composition of the raw material. This variation requires a constant adjustment of the process conditions in order to obtain not only a high pectin yield but also the desired product characteristics. Some of the key pectin characteristics are degree of esterification (DE) and intrinsic viscosity (IV) (Pagán et al., 1999). The target values of these depend on the specific product application.

During extraction pectin yield increases, when temperature increases and pH decreases but temperature and pH also affect DE and IV. Therefore, these process parameters as well as the extraction time must be optimized in order to achieve an optimal compromise between pectin yield and characteristics (Sirisakulwat

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http://dx.doi.org/10.1016/j.jfoodeng.2016.08.006
0260-8774/

et al., 2008).

Statistical models of optimized pectin extraction with respect to yield and DE by response surface methodologies have been reported by numerous researchers, for instance Wai et al. (2009), Masmoudi et al. (2008) and Voragen et al. (2003). First principles models (also referred to as physics-based or white-box models) to predict pectin yield have been studied by Minkov et al. (1996), Panchev et al. (1989) and Durán et al. (2015) in lab scale at constant temperature and pH. Cho and Hwang (2000) combined a kinetic study of pectin extraction with a model of intrinsic viscosity including the influence of temperature on extraction rate constants. The influence of temperature and pH on extraction kinetics has been studied by Pagán and Ibarz (1999). They correlated yields with pH using a third order polynomial. The kinetics of the de-esterification of pectin has been studied by Kirtchev et al. (1989) for extractions at constant pH. There is in the literature a lack of a general first principles model for pectin extraction which couples the reaction and transport phenomena determining the yield of extraction with the functional characteristics of the extracted pectin through IV and DE. For such a model to create value in relation to commercial pectin production methods such a model should describe both the microscopic phenomena at the peel level as well as the overall behavior that can be observed in an extraction tank at scale.

This paper presents a dynamic one-dimensional model of a batch pectin extraction process in order to predict pectin concentration, DE and IV when temperatures and pH vary. The model includes diffusion, reaction kinetics and mass transfer. The rate constants are functions of temperature and pH. A methodology for efficient estimation of the process parameters is proposed and the model is fine-tuned against pilot scale data generated based on a central composite experimental design. In this sense the proposed contribution is in line with the increased focus on first principles modelling and virtualizations in food engineering from the VirProFood meeting in Salerno (2014) and a recent special issue (Vol. 176, 2016) in Journal of Food Engineering as pointed out in the editorial by Marra (2016) and the opening paper by Saguy (2016). The paper is organized with model development and the parameter estimation strategy in the following section, materials and methods in section 3 and results and discussion in section 4 and 5 followed by concluding remarks in section 6.

2. Modelling

In this section a dynamic model of the pectin extraction process is described. The purpose is to describe the main phenomena involved in a batch extraction reactor to predict the effect on yield and pectin properties of changes in the key process conditions: temperature and pH. Balance equations using first principles are utilized to the extent possible to describe phenomena that can be observed at the reactor level. The following simplifying assumptions are made:

1. The peel is considered as a structure where the active component (water insoluble protopectin) is embedded.
2. Water penetrates immediately into the inside of the peel and this leads to release of pectin.
3. Initial concentrations of protopectin and pectin are uniformly distributed in the raw peel.
4. Global reaction and transport coefficients are assumed for the peel.
5. The peels have the shape of flakes with equal size, and are described using a one-dimensional slab geometry.
6. The peel slab geometry is unaffected by the penetration of water.
7. Pectin in the bulk solution is homogenously dispersed as this phase is considered to be well mixed.

The raw peels have been washed with water prior to shipping and during this process pectin has been released from the peels. In the subsequent drying process it is assumed that some of this pectin is re-captured in the peel. Therefore addition of water to the peels results in an initial concentration of water soluble pectin prior to extraction. It is known that the peel morphology consist of several layers which could influence the reaction and mass transport. It is however assumed that a lumped approach to model these as global coefficients for the peel is sufficient in the development of a model for the overall behavior of the leaching process.

The peel flakes are modelled by a one-dimensional slab geometry with a thickness of $2L$. The origin of the x-axis (i.e. $x = 0$) is placed in the centre of the flake so that the exposed surfaces of the flake are respectively at $x = -L$ and $x = L$ (see Fig. 1). The flake is assumed to be symmetric around the centre, and the boundary conditions at $x = -L$ and $x = L$ are identical, therefore the concentration profiles are also symmetric around $x = 0$. This means that $c(x) = c(-x)$ and therefore the system only needs to be solved in the interval from $x = 0$ to $x = L$.

In the peel, acid catalyzed hydrolysis of protopectin takes place and there is internal diffusion of pectin. The proton concentration in the solution is adjusted through addition of a strong acid. There is a mass transport of pectin through the boundary layer to the bulk solution. In the bulk solution, pectin is degraded and ester groups on pectin in the bulk solution may be converted into free acid form. A control volume of thickness Δx along the full height and width of the flake is placed inside the peel between $x = 0$ and $x = L$ in order to describe spatial variation in concentrations in the peel. The acid catalyzed hydrolysis of protopectin:

$$Protopectin(peel) \xrightarrow{[H^+]} Pectin(peel)$$

is assumed to be a first order reaction and therefore this leads to the differential equation:

$$\frac{\partial c_{protopectin(peel)}(t,x)}{\partial t} = -k_{hydrolysis}\left(T, \left[H^+\right]\right) \cdot c_{protopectin(peel)}(t,x) \quad (1)$$

where $c_{protopectin(peel)}$ is the concentration of protopectin in the peel and $k_{hydrolysis}(T,[H^+])$ is the reaction rate of hydrolysis taking into account the temperature and pH dependency. The diffusion of

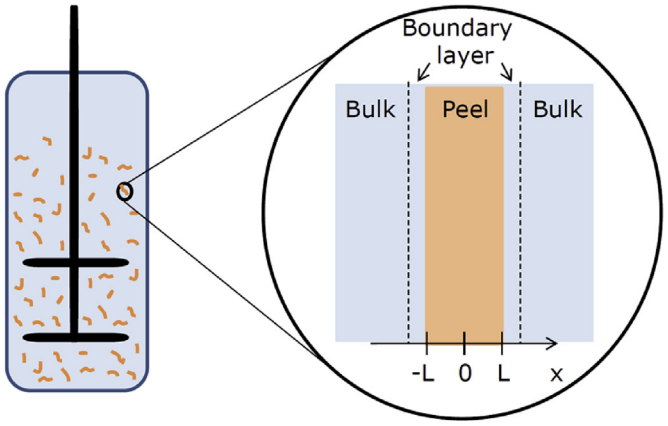

Fig. 1. Batch reactor with peels and the 1D flake model of a single peel.