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Kinetic assessment on the autohydrolysis of pectin-rich by-products

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ABSTRACT

Fractionation in aqueous media is an environmentally friendly technology suitable for obtaining oligomeric products from pectins and hemicelluloses. Sugar beet pulp (SBP) samples were subjected to aqueous processing under non-isothermal conditions to reach maximal temperatures in the range 140–200 °C, in order to cause the conversion of pectins into soluble compounds of lower molecular weight with potential applications as prebiotic ingredients.

Mixtures of arabinooligosaccharides, oligogalacturonides and oligomers made up of other structural units were obtained by non-isothermal processing of SBP in aqueous media. Kinetic models suitable for reproducing and predicting compositional data of reaction liquors as a function of the operational conditions were developed. According to the model predictions, the maximum arabinooligosaccharides yield (15.7 g/100 g SBP) corresponded to a treatment carried out to achieve 171.5 °C. Alternatively, the maximum oliogogalacturonide yield (14.1 g/100 g SBP) was predicted for a treatment performed to achieve 158.2 °C. In both cases, the overall yield of oligomeric saccharides was near to 30 g/100 g dry SBP, whereas the oligosaccharide mixture of higher purity was obtained operating at 158.2 °C. Depending on the operational conditions, SBP processing in aqueous media yielded oligomers with different compositional profiles. The developed models were suitable for a quantitative interpretation of experimental data, and provided key information for both design calculations and economic evaluation.

1. Introduction

The demand of functional ingredients with improved properties has increased in the past few years [1]. The fast growth of the functional food market and the high selling price of prebiotic compounds fosters the search for new raw materials. Alternative, environmentally friendly technologies may play a significant role in the manufacture of new prebiotic ingredients.

Recent studies reported promising perspectives for pectin and pectin-derived oligosaccharides [1–3]. Pectin, a key polymer of vegetal raw materials, includes a family of polysaccharides with common features, but extremely diverse fine structures [4]. Thus, pectin is mainly made up of three structural elements: homogalacturonan (HG), rhamnogalacturonan I (RG-I) and rhamnogalacturonan II (RG-II). HG consists of a backbone of α-(1 → 4)-linked galacturonic acid (GalA) residues, which can be partially methyl-esterified at C-6 and acetyl-esterified at O-2 and/or O-3. RG-I is a ramified polymer made up of chains containing alternate units of galacturonic acid and rhamnose, where arabinan, galactan, arabinogalactan I and II branches can be attached. RG-II is a complex polymer composed of GalA, rhamnose, galactose and some unusual sugars. Fig. 1 shows a schematic representation of pectin, which is widely used as a gelling and stabilizing agent in food technology [5,6]. On the other hand, pectin has medical applications based on its health-promoting effects (including lowering of blood cholesterol and serum glucose levels, potential to cause inhibition of cancer growth and metastasis [7], and ability to modify the surfaces of medical materials [8]).

Currently, citrus peel and apple pomace are the major sources of pectin; whereas sugar beet pulp (SBP) is a potential alternative source. SBP is the spent solid resulting from sucrose extraction of sugar beet with hot water. Sugar beet is an important agricultural raw material, with a world production of 247 millions metric tons in 2007, of which 5.3 millions metric tons were produced in Spain [9]. In a typical sugar beet processing plant, 200 kg of wet SBP (75% (w/w) moisture) are produced from 1 ton of sugar beet. SBP is usually used as a low value component of animal feeds or disposed with an additional cost [10], and the importance of finding new applications for this by-product for the future profitability of the beet sugar processing industry has been pointed out [11].

Abbreviations: AcH, Acetic acid; Acn, Acetyl groups; AcO, Acetyl groups in oligomers; AOS, Arabinooligosaccharides; An, Arabinan; Ara, Arabinose; DP_i, Decomposition products (i = Gan, GaUn, An or Acn); F, Furfural; Gal, Galactose; GalA, Galacturonic acid; Gan, Galactan; GaOS, Galactooligosaccharides; GaUn, Galacturonan; HMF, Hydroxymethylfurfural; OGaU, Oligogalacturonides; OS, Total oligomers; SBP, Sugar beet pulp; Subscript "s", Susceptible fraction; Subscript "RM", Raw material; α_i, Mass fraction of susceptible polymer (i = Gan, GaUn or An).

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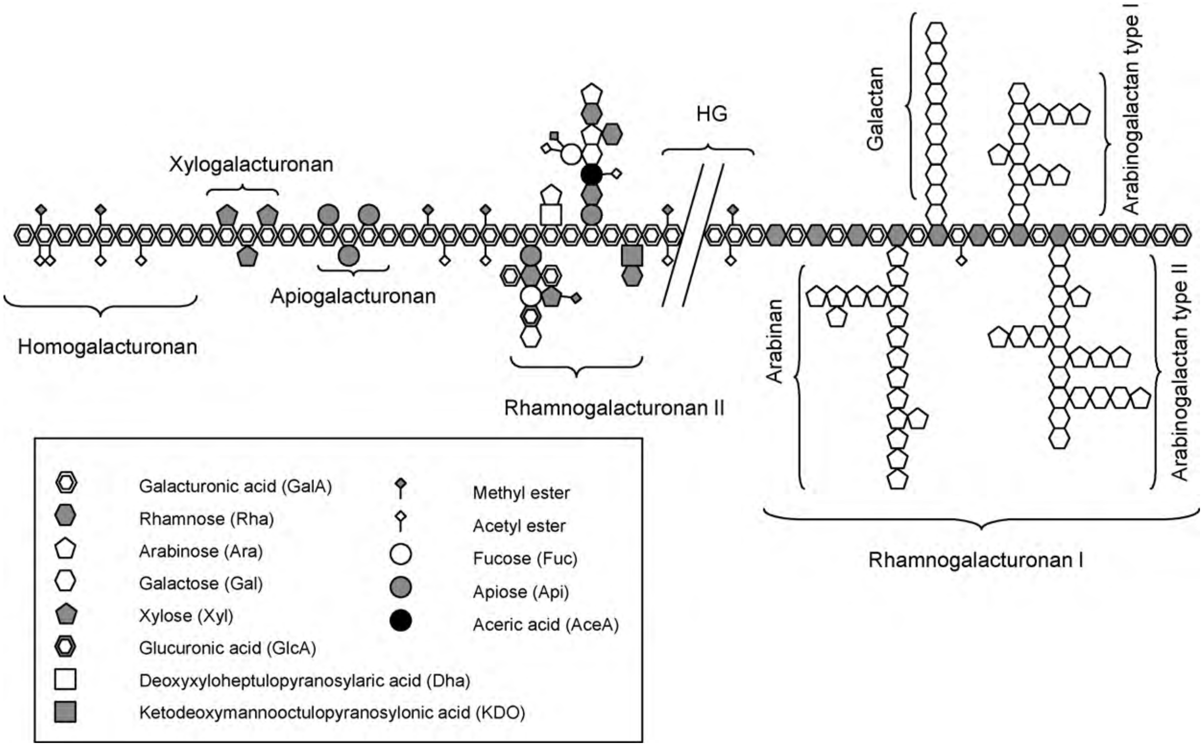

Fig. 1. Simplified structure of pectin.

In recent years, several applications of SBP were considered in literature, including bioethanol [12] or component of green composites [11]. Based on its high pectin content, mainly made up of HG and RG-I [4,13], research studies dealing with the manufacture and application of pectin-derived oligosaccharides have been conducted. Some considered topics include the enzymatic release of ferulic acid and the production of feruloylated oligosaccharides [14–16] or arabinooligosaccharides (AOS), as well as the prebiotic effects of pectin-derived oligomers [10,17].

In a recent work [18], our research group reported on the production pectic-oligomers from SBP by aqueous processing (hydrothermal or autohydrolysis treatments), a technology that shows some favorable features, including: (i) environmentally friendly character (water and feedstock are the only reagents), (ii) ability for generating oligosaccharides in a single stage at high yields, (iii) short reaction time, and (iv) simultaneous production of spent solids enriched in cellulose suitable for further utilization.

Optimization and scaling up of the controlled hydrolytic breakdown of pectic polymers requires the development of kinetic models suitable for predicting the composition of the reaction media achievable under defined operational conditions. To this end, kinetic models describing the non-isothermal autohydrolysis of SBP were developed. The models assumed the contributions of consecutive and parallel, pseudohomogeneous, first-order reactions, and enabled the calculation of media composition under conditions leading to the maximum production of galactooligosaccharides (GaOS), oligogalacturonides (OGaU), AOS or total oligomers (OS). To our knowledge, no studies dealing with the kinetic modeling of the autohydrolysis of pectin-rich materials have been reported.

2. Materials and methods

2.1. Raw material

SBP was supplied by a beet sugar processing industry (Azucarera Ebro, Spain), homogenized in a single lot to avoid compositional differences among aliquots and stored in polyethylene bags at −18 °C until use. Aliquots from this lot were subjected to analytical determinations according to the methodology described by Martínez et al. [18]. The composition (expressed in weight percent oven-dry basis) of the SBP lot used in this work was: 20.1% glucan (Gn), 5.3% galactan (Gan), 1% xylan, 1.4% rhamnosyl moieties, 1.1% mannan, 17.5% arabinan (An), 2.6% acetyl groups (Acn), 21% galacturonan (GaUn), 4.8% klason lignin, 4.5% ash and 10.8% protein.

2.2. Hydrothermal treatments

SBP samples were suspended in water (liquid to solid ratio = 12 g water/g oven-dry pulp) and reacted in a 3.75 L stainless steel reactor (Parr Instruments, Moine, IL, USA) under non-isothermal conditions following the standard heating temperature profile [18] to reach the desired temperatures (140, 150, 160, 163, 165, 167, 170, 180, 190 or 200 °C). At the end of treatments, the reactor was rapidly cooled (to achieve 60 °C), and the liquors were separated from spent solids by pressing. Solids were washed with distilled water and air-dried. Samples from liquors and spent solids were analyzed using the methodology described below.

2.3. Analytical methods

Samples of dried, spent solids were milled to a particle size below 0.5 mm and analyzed using the same methods employed for raw material characterization. Liquors from the quantitative acid hydrolysis of spent solids were analyzed for sugars and acetic acid (AcH) by HPLC using the method described by González-Muñoz et al. [19]. In HPLC chromatograms, galactose (Gal), xylose, mannose and rhamnose were eluted together. Since the Gal content of samples was considerably higher than the ones of the co-eluted sugars, the overall chromatographic peak was quantified and reported as Gal. Uronic acids in liquors were determined by the method of Blumenkrantz and Asboe-Hansen [20].