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Release and recovery of pectic hydrocolloids and phenolics from culled citrus fruits☆

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ABSTRACT

The citrus industry worldwide is threatened by a bacterial disease (Huanglongbing, HLB) spread by a sap sucking hemipteran, the Asian citrus psyllid (*Diaphorina citri*). Before tree death there is a period of increased preharvest fruit drop and the production of smaller fruit containing off-flavored juice. The increasing frequency of HLB symptomatic fruit moving into the juice processing chain may become a challenge for maintaining flavor quality. An alternative use is sought for flavor degrading fruits, to recover value for fruit growers and juice processors. The purpose of this study was to investigate a steam explosion process for the release and recovery of highly functional pectic hydrocolloids and phenolic compounds from culled fruit. Symptomatic fruit from two varieties were culled and either entire fruits or juice-extracted fruit peels were submitted to steam explosion. Released pectic hydrocolloids, a useful hydrocolloid readily functionalized via alkaline demethylesterification, were co-isolated with a solvent-free fraction enriched in phenolic compounds. Recovery of pectic hydrocolloids ranged from 58% to 78%. Weight average molecular weight of this material ranged from 5.78×10^5 to 1.02×10^6 kDa and the degree of methylesterification ranged from 61% to 79%. Functionalization using alkaline, calcium sequestering compounds resulted in viscosities up to 250 mPa s^{-1}. Additionally, recovery ranges of 5%–100% of the polymethoxylated flavones, 2%–71% of the flavanone glycosides, >50% of the limonoids were obtained. These results indicate this process would be useful for recovering value from culled fruit which would otherwise either degrade juice quality or be shunted for conversion to low value animal feed.

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1. Introduction

Huanglongbing (HLB) is a bacterial disease that has spread throughout the citrus growing regions of Florida, and much of the citrus cultivating regions in the world (Choi, Lee, Ehsani, Schueller, & Roka, 2016; Gottwald, 2010). In addition to tree decline and eventual death, the harvestable yield decreases due, in part, to preharvest fruit drop (Albrigo & Stover, 2015). Furthermore, the fruit size becomes smaller and juice quality deteriorates (Baldwin et al., 2010; Plotto et al., 2010; Raithore et al., 2015). As HLB becomes more and more widespread, HLB symptomatic fruit from sweet oranges will comprise an increasing proportion of citrus fruit targeted for juice extraction. Concomitant with this will be a degradation of juice flavor. If the ratio is greater than 3:1 symptomatic vs. non-symptomatic juice the off flavors present in juice from symptomatic fruit can be perceived by sensory analysis (Raithore et al., 2015). One potential remedy is to cull the HLB symptomatic fruit prior to juice extraction in an effort to prevent

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overall juice quality degradation. However, this would have its own economic impacts on citrus growers and the juice processing industry. An option is to enable the production of alternative value-added products from these fruits. Two valuable, functional components present in citrus fruits are the pectic hydrocolloids and the wide array of phenolic compounds. Juice extracted citrus fruits (mainly peel, segment membranes and central core tissues) contain 15%–20% pectic hydrocolloids (Grohmann, Cameron, & Buslig, 1995; Grohmann, Cameron, Kim, Widmer, & Luzio, 2013) and 4%–6% phenolics (Cameron, Chau, & Manthey, 2016) on a dry weight basis.

Pectic hydrocolloids are highly functional molecules, having the ability to modify the rheology of aqueous systems (Chan, Choo, Young, & Loh, 2016), to serve as ion capture agents (Iqbal, Schiewer, & Cameron, 2009) and to control hydration (Zsivanovits, MacDougall, Smith, & Ring, 2004). Pectin is a complex polysaccharide commonly recognized as having two major regions, homogalacturonan and rhamnogalacturonan I (Atmodjo, Hao, & Mohnen, 2013). Rhamnogalacturonan II also is present but comprises a much smaller proportion of the total pectic sugars. Homogalacturonan is a linear polymer of α-1,4 linked galacturonic acid (GalA). Rhamnogalacturonan I (RG I) is a generally shorter copolymer of a repeating dimer of rhamnose and galacturonic acid. Arabinans, galactans and arabinogalactans are attached as side chains to rhamnose sugars in the RG I regions. Functionality of pectin is largely determined by the amount of methyl esters on C6 of GalA in the homogalacturonan region, the distribution of these charges and the average molecular weight of the polymer. Commercial pectin production currently relies heavily on citrus peel (May 1990; Rolin, 2002; Staunstrup, 2009). A hot, acid extraction process followed by alcohol precipitation is the common practice to obtain food grade pectin. Expenses associated with this extraction process preclude the use of pectin in many potential applications. Additionally, phenolics are not recovered by this process.

Phenolics are low molecular weight compounds containing at least one aromatic ring and are a very diverse group of biological molecules (Balasundram, Sundram, & Samman, 2006). Some of these phenolic compounds have been shown to possess bioactivity. The dominant phenolic compound in sweet orange fruits, as well as lemons and limes, is hesperidin (Peterson et al., 2006) and more phenolics are found in inedible fruit peel vs. edible portions (Gorinstein et al., 2001). Following consumption of citrus a number of hesperidin and narirutin (also prevalent in sweet oranges) metabolites have been identified in humans and have been shown to be powerful mediators of gene activation in inflammation and other chronic human diseases (Bredsdorff et al., 2010; Brett et al., 2009; Vallejo et al., 2010). Hesperidin is commonly recovered from citrus juice processing waste by crystallization following alkaline treatment, pressing and liquid neutralization (Baier, 1948). Unfortunately, the other remaining phenolics and limonoids, as well as pectic hydrocolloids are lost during this process.

For these two components of citrus fruits to become valuable coproducts from culled HLB symptomatic fruit, a method to release them from their intercellular entrapment, retain their individual functionalities and to readily recover them using a simple technology is needed. Previously we have demonstrated a simple method to recover both pectic hydrocolloids and phenolic compounds from juice extracted citrus peel (Cameron et al., 2016). In this study, using a pilot scale, continuous steam explosion process followed by a simple water wash, we were able to recover an average of 72% of the pectic hydrocolloids, 41% of the polymethoxylated flavones, 11% of the flavanone glycosides, 85% of the limonoids and 100% of the hydroxycinnamates present in juice extracted citrus peel.

Here we report on the application of this “Green” methodology for the release and recovery of these pectic hydrocolloid and phenolic materials from culled, HLB symptomatic fruit. Both mid-season and late season varieties were utilized and both whole, intact fruit as well as juice extracted fruit peel were submitted to steam explosion.

2. Materials and methods

2.1. Materials

Culled, HLB symptomatic citrus fruit from varieties ‘Midsweet’ and ‘Valencia’ were obtained from a local citrus juice processor. Juice extracted peel was obtained by juicing an aliquot of the fruit in a JBT Food Tech Fresh’n Squeeze® Point-of-Sale Juicer the same day as the fruit were obtained. Both intact fruit and juice extracted peel were refrigerated overnight at 4 °C and submitted to steam explosion the following day.

2.2. Steam explosion

In separate runs either whole, intact fruit or juice extracted peel was fed into a receiving hopper and then transferred via a high solids pump into an enclosed tube (Fig. 1). Steam was injected into the biomass stream using a jet cooker (Stewart, Widmer, Grohman, & Wilkins, 2013). The biomass stream was held under pressure at approximately 0.34–0.38 MPa (≈150 °C) by pumping through a hold tube of sufficient length to maintain the temperature and pressure for 1–3 min. Pressure was monitored after the addition of steam and maintained via an adjustable valve at the end of the hold tube to control back pressure. The pressurized biomass was vented into a flash tank at atmospheric pressure where decompression serves to reduce particle size. The steam-exploded biomass was then pumped into resealable plastic bags and stored frozen at −20 °C (see Fig. 2 for schematic diagram).

2.3. Sugar composition of pectic hydrocolloids in raw and steam-exploded biomass

Samples of raw and steam-exploded biomass were enzymatically hydrolyzed in 50 mmol L^{-1} sodium acetate buffer, pH 4.8 using an excess of pectinase (Pectinex Ultra SPL), cellulase (Celluclast 1.5L) and B-glucosidase (Novozyme 188) enzymes for 24 h at 45 °C and the dominant pectic hydrocolloid sugars were quantified via high performance anion exchange chromatography coupled to a pulsed Amperometric detector (Grohmann et al., 2013). Additionally, soluble sugars were quantified following a simple water wash without using an enzymatic hydrolysis. Insoluble and soluble solids were quantified by filtration and drying (Widmer, Zhou, & Grohmann, 2010).

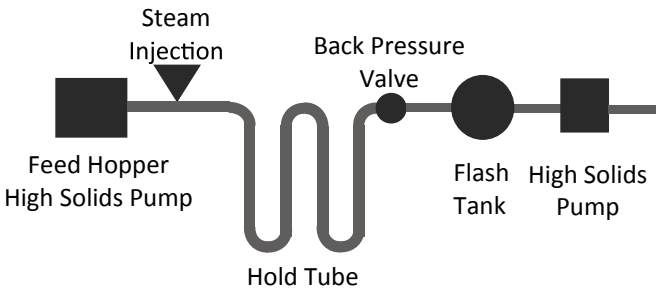

Fig. 1. Schematic representation of steam explosion system.