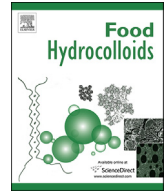




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Thermal degradation of citrus pectin in low-moisture environment - Influence of acidic and alkaline pre-treatment

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ABSTRACT

Pectin powder is degraded during storage and transport by demethoxylation and depolymerisation. The degradation mechanisms and especially the influence of pre-treatments on the degradation reactions are not completely understood. In this study, commercial citrus pectin was modified by either acidic or alkaline demethoxylation. The modified pectins, as well as the commercial pectin, were thermally degraded during four weeks of storage at 60 °C and 80% relative humidity. Demethoxylation and depolymerisation as well as colour alterations were examined during degradation, and the course of the reactions was monitored.

It was found that the type of pre-treatment during modification determined the material properties and, thus, the water uptake of the modified pectin powders. The resulting water availability in the samples was crucial to the extent of demethoxylation and to the type and intensity of depolymerisation since some of these reactions competed for the water in the climate chamber. The pre-treatment also determined the content of neutral sugars and sodium ions of the modified pectins. High contents of these components limited the extent of degradation in different ways.

A previously assumed third depolymerisation mechanism of pectins, beside backbone hydrolysis and β -elimination, was confirmed.

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1. Introduction

Pectin is one of the most popular food ingredients worldwide and, in contrast to other hydrocolloids, has an excellent image. Commercial pectins are produced as powders mainly in Europe (Germany, Denmark, France) and, to a lower extent, in Latin America and China. They are sold and applied worldwide and have to be transported and stored for several weeks or months, often under unfavorable environmental conditions. Such storage may cause pectin degradation (Einhorn-Stoll & Kunzek, 2009; Einhorn-Stoll, Benthin, Zimathies, Görke, & Drusch, 2015a; Einhorn-Stoll, Kastner, & Drusch, 2014; Padival, Ranganna, & Manjrekar, 1981). Pectin is degraded also by heat-processing as was found in pectin-containing plant tissues and in food products such as fruit juices, purees and jams (for instance Christiaens et al., 2011; Ibarz, Garza, & Pagán, 2008; Sila, Smout, Elliot, Van Loey, & Hendrickx, 2006;

Jayaraman & Van Buren, 1972). The thermal degradation causes non-enzymatic browning and has an impact on the product quality.

Pectin degradation has been investigated in the last decades mainly in model pectin solutions. Several groups tested the influence of external factors such as temperature and pH and of internal parameters such as degree of methoxylation (DM) and of ions (for instance Bornik & Kroh, 2013; Diaz, Anthon, & Barrett, 2007; Fraeye et al., 2007; Krall & McFeeters, 1998; Renard & Thibault, 1996; Axelos & Branger, 1993; Sajjaanantakul, Van Buren, & Downing, 1993; Kravtchenko, Arnould, Voragen, & Pilnik, 1992; Voragen, Schols, & Pilnik, 1988; Thibault, 1983; Van Buren, 1979; Keijbets & Pilnik, 1974; BeMiller & Kumari, 1972). Most works did, however, not consider a possible influence of pectin pre-treatments or of different production details on the thermal degradation reactions. For instance, demethoxylation is possible by enzymatic or by chemical treatments at low pH (acidic demethoxylation) as well as at high pH (alkaline demethoxylation), what is leading to considerable differences in pectin composition and material properties (Einhorn-Stoll, Kastner, Hecht, Zimathies, & Drusch, 2015b).

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The knowledge of thermal pectin degradation in solutions may only to some extent be transferred to pectin powder. In comparison to solutions, dry pectin powder is assumed to be in a relatively stable state. Nevertheless, it is a highly reactive system, especially at high temperature and humidity. First investigations on the influence of long-term storage on dry pectin powders have been reported by Padival et al. (1981). They stored different low-methoxylated pectin (LMP) samples at room temperature for up to 12 months and found a certain degradation by demethoxylation and depolymerisation. Einhorn-Stoll and Kunzek (2009) accelerated the degradation of different lab-prepared high-methoxylated pectin (HMP) and LMP powders by storing samples in a climate chamber at 50–60 °C and 60–80% relative humidity for two weeks. Beside demethoxylation and depolymerisation, all samples showed a visible browning. Discussing the possible degradation mechanisms, an additional third depolymerisation reaction beside the well-known backbone hydrolysis and β -elimination was assumed. Based on these results, the degradation of commercial pectins of varying types and from different suppliers was examined (Einhorn-Stoll et al., 2015a; Einhorn-Stoll et al., 2014). According to all these works, the intensity of the thermal pectin degradation was dependent on not only temperature and relative humidity in the system but also on the pectin type and molecular parameters. Padival et al. (1981) described a slightly stronger degradation of acidic treated compared to alkaline treated modified LMP. Einhorn-Stoll and Kunzek (2009) found an influence of the initial DM of the modified pectin. Since pectins with similar molecular parameters such as DM or intrinsic viscosity ($[\eta]$) but from various suppliers differed strongly in their degradation behavior, Einhorn-Stoll et al. (2015a, 2014) additionally assumed an impact of the raw material (type and geographic source of citrus fruits) and of the production process as described before for other food powder properties (Cuq, Rondet, & Abecassis, 2011). As a consequence, for a systematic investigation modified pectin types should be prepared by different procedures from one single initial sample.

The presented study shall examine the thermal degradation of pectin powder (thermolysis) more detailed and in dependence on different pre-treatments applied for pectin modification. It is using citrus pectin since about 80% of all industrially applied pectins are of citrus origin. In comparison to the previous studies, the storage in the climate chamber was extended to four weeks and not only the final but also intermediate states have been examined. The aims were (1) to investigate the influence of type of pre-treatment and intensity of pectin modifications on the thermal degradation of pectin powder, (2) to study the course of these reactions and (3) to understand the complex mechanisms of the involved degradation reaction types.

2. Theoretical background

In order to understand the degradation reactions, it is necessary to remember the pectin molecular structure as described in detail by several authors (for instance Schols & Voragen, 2002; Thakur, Singh, & Handa, 1997). In the most common model, pectin consists of a backbone of galacturonic acid molecules (GalA), which are connected via glycosidic linkages and are partly methylesterified at C6 (homogalacturonan section). The GalA is partly linked with rhamnose molecules (rhamnogalacturonan section) to which neutral sugar side chains are bound. These chains contain for instance D-galactose (Gal), D-glucose (Glu) or L-arabinose (Ara) as shown in Fig. 1. According to the DM of the GalA, the pectins are divided into HMP and LMP.

In the last decades, many authors have intensively examined the influence of the reaction conditions pH and temperature and the impact of pectin DM on thermal pectin degradation in solutions

with regard to possible mechanisms, interactions and reaction products. They found that the typical degradation reactions are demethoxylation as well as depolymerisation by backbone hydrolysis and/or β -elimination (Fig. 1). The dominating reaction types depended on several factors:

- High DM favours β -elimination since adjoining ester groups are necessary for this reaction. Thus, demethoxylation indirectly reduces a parallel depolymerisation by β -elimination (Albersheim, Neukom, & Deuel, 1960; Diaz et al., 2007; Fraeye et al., 2007; Keijbets & Pilnik, 1974; Krall & McFeeters, 1998; Van Buren, 1979).
- Low DM promotes backbone hydrolysis. Pectin demethoxylation indirectly enhances this depolymerisation reaction (Diaz et al., 2007; Fraeye et al., 2007; Krall & McFeeters, 1998; Timell, Enterman, Spencer, & Solters, 1965).
- Substituents bound at C-5 of the GalA have a considerable influence on backbone hydrolysis. Glycosidic linkages between glycosiduronic acids (-COOH at C-5, such as galacturonic acid) are more resistant to acid hydrolysis than glycosidic linkages between glycopyranosides (neutral sugars) because of an inductive effect of the carboxyl group at C-5 and/or because of conformational reasons (BeMiller & Doyle, 1971; Timell et al., 1965; Van Buren, 1979). It was partly assumed, therefore, that backbone hydrolysis takes place mainly in the rhamnogalacturonan fraction (Van Buren, 1979). The hydrolysis resistance of the linkages in the backbone is additionally increased by bound methoxyl groups (-COCH₃) instead of carboxyl groups at C-5 in pectins with high DM.
- Low pH around or below the pK_a of pectin (at pH 3.5) favours acidic demethoxylation and acidic backbone hydrolysis. The reaction rate of acidic demethoxylation is higher than that of acidic backbone hydrolysis (Timell et al., 1965). pH above 6 promotes alkaline demethoxylation (saponification) and β -elimination. In the intermediate range all these reactions have been detected (Diaz et al., 2007; Fraeye et al., 2007; Krall & McFeeters, 1998) to different extents.
- Neutral sugars in side chains are cleaved hydrolytically, especially at acidic pH. This reaction is favoured over backbone hydrolysis (Axelos & Branger, 1993; Van Buren, 1979).
- Cations are assumed to support the degradation by β -elimination (Keijbets & Pilnik, 1974; Sajjaanantakul et al., 1993) but have no effect on backbone hydrolysis (Krall & McFeeters, 1998).
- High temperature accelerates all degradation reactions but in particular β -elimination (Diaz et al., 2007; Fraeye et al., 2007; Kravtchenko et al., 1992).

The reaction products give information about the dominating type of degradation reactions. Acidic backbone hydrolysis produces only reducing sugars but β -elimination additionally forms unsaturated uronides, which later on often cause non-enzymatic browning (Diaz et al., 2007).

Some important differences between dissolved pectins and pectin powders have to be considered for the investigation of thermal degradation processes:

- Pectin powders are complex systems with specific characteristics (Cuq et al., 2011) not only depending on the chemical composition but also on the material properties. The more or less compact structure of the pectin powder particles is crucial to the extent of adsorption and absorption of water for the degradation reactions (Einhorn-Stoll et al., 2015a, b).
- Even if the surface of the particles is softening and partly starting to dissolve at high relative humidity (Basu, Shivhare, & Muley, 2013; Matveev, Grinberg, & Tolstoguzov, 2000), in

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