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Pectin production and global market

KEYWORDS: Pectin, waste citrus peel, biopolymer, biorefinery, bioeconomy.

Abstract Pectin is a valued hydrocollid with multiple functional properties applied in the food, cosmetic and pharmaceutical industries. In this study we describe pectin, its properties and sources, and identify the main market trends, drivers, and open opportunities.

INTRODUCTION

Pectin is a ubiquitous natural polymer found in the primary walls of non-woody plant cells, whose large and increasing use as hydrocolloid (a substance capable to trap water and to form gels at low concentration) by the food industry is rapidly expanding into other industrial sectors (1). Even in the food sector, traditional usage as a gelling agent, thickening agent and stabilizer is being complemented by the emerging utilization of pectin as a fat replacer and health-promoting functional ingredient (2).
Today mainly obtained from citrus and apple peel, pectin is a block co-polymer comprising 1,4-α-linked galacturonic acid and 1,2-linked rhamnose with side branches of either 1,4-linked β-D-galactose or 1,5-α-linked L-arabinose (Figure 1).

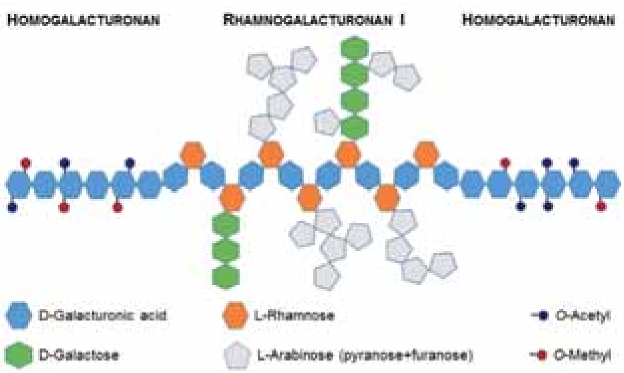

Figure 1. Pectin schematic structure.
(Reproduced from Ref. (3), with kind permission)

Some of the C-6 carboxyls of the galacturonic acid backbone are esterified with methoxyl groups, while others are present as uronic acid salt giving to pectin dissolved in water excellent metal chelating properties. The gel-forming ability of pectin is due to the ease of association of pectin chains in water, leading to the formation of a three-dimensional network comprised of long segments of galacturonic acid moieties, interrupted by the incorporation of rhamnose and branching of the chain. Association usually occurs by the formation of intermolecular junction zones between two or more homogalacturonic chains. In general, high content of galacturonic acid and low degree of methyl esterification promote the availability of COO^- groups, involved in the gelling process (4).
From a functional viewpoint, pectin has excellent water binding and gel forming properties even at low concentration. For this reason, it is widely used as thickener and stabiliser in the food industry (extracted pectin, E440, Figure 2) as gelling agent in jams, confectionary, and bakery fillings, and as stabilizer in yoghurts and milk drinks. Other relevant uses are in the cosmetics, personal care (paints, toothpaste and shampoos) and pharmaceutical (gel caps) sectors, including new utilization as nutraceutical ingredient (5).
Since the early 2000s, indeed, it has become increasingly clear that pectin has several beneficial health and nutritional effects as a dietary fibre and prebiotic. In 2010 the European Food Safety Authority (EFSA) recognized the scientific validity of nutrition and health claims regarding pectin as a nutritional supplement in the reduction of post-prandial glycaemic responses, the maintenance of normal blood cholesterol concentrations and the increases in satiety, leading to a reduction in energy intake (6). Conventional producers of pectin, which had been hesitant about promoting the potential nutraceutical effects of their products (7), were suddenly confronted with an unexpected outcome, *i.e.* the use of pectin as a health ingredient.

In 2012 Maxwell and co-workers published a comprehensive account on the emerging bioactive properties of pectin (8). More recently, we have described pectin extraction and applications put in the context of the emerging biorefinery (9).
The study provided a unified view of the main research and utilization trends, and concluded that pectin will shortly emerge as a central bioeconomy product, leading to expanded production, with new extraction methods replacing obsolete hydrolysis of protopectin in hot water with dilute mineral acids, and recurring to new natural sources beyond citrus and apple peels, such as coffee pulp (10). Though annually investigated by market research consultancies (11), an insight into the pectin's global market in the open scientific literature will be useful to researchers, managers and entrepreneurs in light of the increasing importance and constant growth, in production and utilization of this natural product. In the following we identify the main market trends, drivers, and open opportunities.

SOURCES

Today pectin is mostly (85%) produced from citrus peels (56% from lemons, 30% from limes, and 13% from oranges), and from apple pomace (14%), with a minor fraction being obtained from sugar beet. Pectin for use in food is defined as a polymer containing at least 65% galacturonic acid units.
After juice extraction, essential oil and dissolved sugars are removed from the peel prior to drying. Prior to pectin extraction with dilute mineral acids, the citrus peel must be dried from the starting level of about 82% moisture, down to 10 to 12% moisture to avoid fermentation. Because of the high water content and the perishable nature of the waste, drying is only economically viable on-site or nearby to the citrus processing plant, and only where large amounts of waste accumulate.
In detail, after pressing the citrus fruit to extract the juice, citrus processors wash the peel to remove essential oil and dissolved sugars, and gently dry the peel at temperature not exceeding 110°C (12). Rotary or direct fire dryers are normally used, avoiding direct contact between the flame and peel. The world's largest producers of dried citrus peel are in Argentina and Mexico but producers are located also in Peru, Spain and Bolivia. In South America and in Sicily pectin is often extracted directly from the wet citrus peel, immediately after juicing.
Brazil and Mexico use orange and lime peel as the main pectin's raw material. while current production in Germany mainly relies on apple pomace. Regardless of the type of raw material, however, the current manufacturing process is based on extraction via acid hydrolysis in hot water. In order to control polymeric degradation, both the pH and hydrolysis time need to be checked carefully.
Protopectin in the washed and dried citrus peel is solubilized with a dilute mineral acid (HCl or HNO_3 or H_2SO_4) at pH 2-3, for several hours at 50-100°C. Following separation from the spent peel, the pectin extract is filtered and precipitated with alcohol (isopropyl alcohol). The alcohol is recovered by distillation while pectin is washed, dried and sold in powder from. Common yields of pectin are ~ 3% of the wet peel weight (13).

Figure 2. Pectin extracted in powder form from citrus peel. (Reproduced from Wikipedia, with kind permission).

When pectin is extracted with acid, much of the rhamnogalacturonan "hairy" regions of the polymer are destroyed, leaving mainly the galacturonic acid "smooth" regions, with a few neutral sugar units attached or in the main linear chain.
As expected, the chemical characteristics of the extracted pectin depend upon the extraction conditions and the sourcing material. For example, pectin from sugar beets has hydrophilic and hydrophobic regions and is commercialized as organic surfactant for use in the stabilization of juices and dressings. The degree of esterification and the distribution of the carboxyl groups in the pectin polymer correlate with the gel setting rate and gel texture under otherwise similar conditions. Due to a blockwise distribution of carboxyl groups (14), citrus pectins with the same degree of esterification will form gels with a slightly higher setting temperature and a more elastic texture when compared to apple pectins. The same blockwise carboxyl groups distribution of high methylester (HM) pectins additionally provides advantages regarding protein stabilization in acidified milk drinks.

MANUFACTURERS

Production of pectin started in Germany in 1908 when producers of apple juice started to cook dried apple pomace, the main by-product from the apple juice manufacture. The extracted pectin was sold as gelling agent. Demand was high, and in the 1930s the process was industrialized by new companies such as *Opetka*, *Obipektin* or *Herbstreith & Fox* at new industrial sites established close to producers of apple juice. Production started shortly afterwards also in the United States and continued until the early 1990s when it was relocated to Mexico (and Brazil), as the environmental regulation of pectin's plants in the US was made considerably stricter.
The cumbersome acid hydrolytic process to isolate pectin from citrus peel on industrial scale, indeed, is one of the most revealing examples of the obsolescence of industrial extraction processes. This extraction process generates such large amounts of acid wastewater, that the high cost to comply with disposal costs enforced in the US in the early 1990s, complelled manufacturers (one in California and the other in Florida) to relocate pectin production plants in Mexico (15).
Conventional pectin extraction factories are generally expensive, and require a close, large-scale source of raw material, namely dried citrus peel or apple pomace. Under these conditions it is perhaps not surprising to notice that the pectin market for decades has been heavily consolidated, with six main producers responsible for most of the output (*Herbstreith & Fox, Naturex/Obipektin, Danisco/Dupont*, *Cargill, CP Kelco, Yantal Andre Pectin*).

CP Kelco has plants, in Denmark and Brazil. *Danisco* (DuPont) has plants in Mexico and Europe. *Cargill* has plants in Germany, France and Italy, whereas *Herbstreith & Fox* operates only in Germany. Established in 2003 in China, *Yantal Andre Pectin* was the first company in two decades to build a new large plant to manufacture apple and citrus pectin. Pointing to increasing competition and production levels, however, since then several new companies have entered the market, including both new manufacturers and large specialty chemicals makers.

MARKET TRENDS AND USES

In only one decade, annual sales of *Yantal Andre Pectin* reached €30 million, and the company today is one of the world's largest. Similarly, *CP Kelko* between 2011 and 2015 increased the company's production capacity by more than 50% at its pectin manufacturing facilities in Denmark and in Brazil.
In 2009 a technologist at a primary pectin manufacturer quantified the pectin market at 30,000 tonnes (including 5,000 tonnes of low methoxyl (LM) pectin). The overall annual growth rate was reported to be 6% with prices esteemed at $11.00/kg for HM pectin and $12.90/kg for LM pectin (16). Yet, in 2013 a leading chemical magazine reported that the global pectin market had reached $850 million (17). In 2015 the average price exceeded $15/kg and the market, exceeding 60,000 tons, was close to reach $1 billion (18).
Growth is driven by rising demand for functional food products, which translates into expanded market for hydrocolloids (19), as well as increasing use by the cosmetic and pharmaceutical industries.
The food industry's demand for low-calorie and low-fat food products from consumers has resulted in increased demand for pectin from food manufacturers. Being an hydrocolloid, pectin disperses in water and can act as a fat replacer in processed food.
Moreover, pectin is widely and increasingly used in the food industry, to add desirable texture to foods and beverages, but also as dairy replacer and as active ingredient in functional foods, broadening its application scope (pectin has the GRAS status and in the US, it is an approved food additive in the EU coded E440). Indeed, in the last decade, pectin has become an essential additive in the production of yogurts, soy drinks, and juice fruits, to stabilize acidic proteins during heat processing.

In cosmetic and in personal products, besides its use as natural texturizer for ointments, oils and creams, and as an effective thickener and stabilizer for shampoos, lotions and hair tonics, pectin is now used as an effective skin anti-aging agent (20).
In medicine, pectin is used in wound healing preparations and in specialty medicine adhesives such as colostomy devices. Pectin is a natural part of the human diet, and its intake is highly beneficial as pectin binds to cholesterol in the gastrointestinal tract (reducing blood cholesterol levels), and slows glucose absorption by trapping carbohydrates (21).
Numerous drugs are encapsulated within a pectin film to protect the gastric mucosa and to allow sustained release of the active ingredient into blood (22).
Another rapidly emerging use of pectin is to detoxify the body from heavy metals, including radioactive isotopes such as ^{137}Cs in contaminated areas such as Fukushima, in Japan, or Chernobyl, in Belarus and Ukraine. For example, from 1996 to 2007 a total of more than 160,000 Belarussian children received pectin food additives (5 g twice a day) during 18 to 25 days of treatment. As a result, levels of ^{137}Cs in children's organs decreased after each course of pectin additives by an average of 30 to 40%. Belarus scientists concluded that consumption of pectin-based food additives and drinks (using apples, currants, grapes, sea seaweed, etc.) is one of the most effective ways for individual radioprotection (23).
Lately, a number of nutraceutical products (*Pecta-Sol*, *ProPectin* etc) based on modified citrus or apple pectin have entered the market. Modified pectin rich in galactose residues, a far more soluble form of pectin (MW from 100,000 to 5,000-10,000 Daltons), was originally (1992) (24) obtained by means of high pH and temperature treatment. However, nowadays it is more precisely obtained via enzymatic hydrolysis, through which pectin is partly hydrolysed, affording shorter chain pectin molecules that are more easily absorbed in the intestinal tract. Some of these nutraceutical products such as *Pecta-Sol* have undergone numerous rigorous clinical trials (25), even though reviewing the medical uses of pectins in 2011, Endress reported that he had not been able to synthesize modified citrus pectin (1).

OUTLOOK AND CONCLUSIONS

Pectin is a versatile hydrocolloid polymer whose market is rapidly expanding both in conventional and new application segments. On the one hand, the market is growing rapidly, driven by increasing consumer demand for low-calorie, high quality food products. Yet, beyond this advantage in the food industry, pectin gives firmness to many food products consumed on a daily basis (jam, yogurt, ice cream, gravy, salad dressing and several others). In doing so, thanks to its good palatability, pectin blends with food without affecting the flavor of the base material.
Furthermore, pectin utilization has significantly expanded in the cosmetic, pharmaceutical and nutraceutical industries.

The overall result is that in the last decade (2005-2015), despite increases in the raw material prices and shortages of raw material supply (especially of dried citrus peel), there has been a constant growth of the pectin market, leading to significant production capacity expansion.
The global market has gone from 30,000 to 60,000 tonnes per year, and counting. New players, such as *Jin Feng* Pectin in China now producing 1,000 tonnes, have entered the market. Furthermore, new producers using different raw material, such as *Pectcof* in the Netherlands, started production, though still on small scale.
Pectin then, exactly like what happened with glycerol in the polyol market (26), will replace a number of hydrocolloids that have been used on large scale due to their much lower cost. This, inter alia, explains why reputed market analysts predict that pectin market will double by 2020, with sales forecasted to exceed $ 2.4 billion (27).
This growth trend, we forecast in conclusion, will continue, until new extraction methods will make pectin extraction easier, further lowering barrier to new entrants. We remind here that the costs of compliance to dispose of the large volume of waste generated during pectin conventional production were found to be so high that, when in the US the Environmental Protection Agency passed new regulation in the early 1990s, the last US-based pectin production plant was relocated from Florida to Mexico (15).
New research has lately resulted in new extraction processes that challenge conventional production to meet the increasing demand and need of pectin production due to increased uses. We and others recently described the first scalable eco-friendly process for the simultaneous extraction of pectin and the essential oil *d*-limonene from wet lemon peels (28). To test whether the new process would be compatible with kilograms of material, a first method included adding water to wet lemon peels, doing a microwave hydrodistillation, separating the essential oil from the residual water, and finally freeze-drying the water to obtain pure pectin.
In brief, adding 36 L of water to 20 kg of waste lemon peels produced 3 kg of pectin and 10 mL of essential oil. For comparison, common yields for pectin from the conventional extraction method are only roughly 3% of the peel weight, namely 20 kg of lemon peels produce about 0.6 kg of pectin. We then used microwave hydrodiffusion and gravity (29), where the lemon peels and water are heated using microwaves and the residual liquid that is expelled by heating is passed through a filter and condenser to be collected. The collected aqueous solution is then freeze-dried to obtain pure pectin. Besides significantly better yields of pectin no acid is employed. This, along with microwave heating requiring less time than normal heating, minimizes degradation of pectin. As microwave extraction processes of natural products are eventually finding industrial application (30), the route seems open to rapid innovation in conventional extraction of this valued heteropolysaccharide.

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