

Pectin: A new perspective from the biorefinery standpoint

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Abstract: Pectin is a natural product of central importance in the emerging biorefinery that uses fruit waste as a raw material. Generally obtained from lemon peel or from apple pomace, pectin is mainly used as a thickener and a stabilizer in the food industry. Due to its unique chemical properties and biochemical activity, however, its use is growing in many other sectors. Providing a unified view of the main research and utilization trends, this study identifies open opportunities toward larger scale production of a valued biopolymer that, we argue, will shortly emerge as a central product of the biorefinery, and of the citrus-based biorefinery in particular. © 2015 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: pectin; waste citrus peel; biopolymer; biorefinery; bioeconomy

Introduction

Dubbed ‘pectic acid’ after the Greek word $\pi\eta\chi\tau\epsilon\varsigma$ (*pektes*) for ‘coagulated material’, by Henri Braconnot in 1825, while continuing the studies of the gel-forming substance isolated from apple juice by Vauquelin in France in 1790, pectin is a heteropolysaccharide 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- (Fig. 1).¹ In addition, some of the C-6 carboxyl units of the galacturonic acid backbone are esterified with methoxyl groups, or exist as uronic acid salt.

In general, the pectin polymer contains between 300 and up to around 1000 saccharide units (150 kDa molecular weight).

Pectin is the main component of the primary walls of non-woody plant cells, and is abundant in most vegetables and fruit imparting strength and flexibility to the cell wall,

besides having a number of fundamental biological functions (signaling, cell proliferation, differentiation, and cell adhesion).¹ The rhamnose-rich regions of pectin chains enhance molecular interactions between cells and the polysaccharide, while the branched galactose-rich hairy regions promote the formation of entangled structures.³

From a functional viewpoint, pectin is a hydrocolloid, namely a substance capable of trapping water and forming gels at low concentration. Being soluble in water and thanks to its excellent health and safety profile, pectin is widely used for adding a desirable texture to food and beverages. In 2010, the European Food Safety Authority recognized the scientific validity of nutrition and health claims regarding pectin as a nutritional supplement in the reduction of post-prandial glycemic responses and the maintenance of normal blood cholesterol concentrations. It also increases satiety leading to a reduction in energy intake.⁴

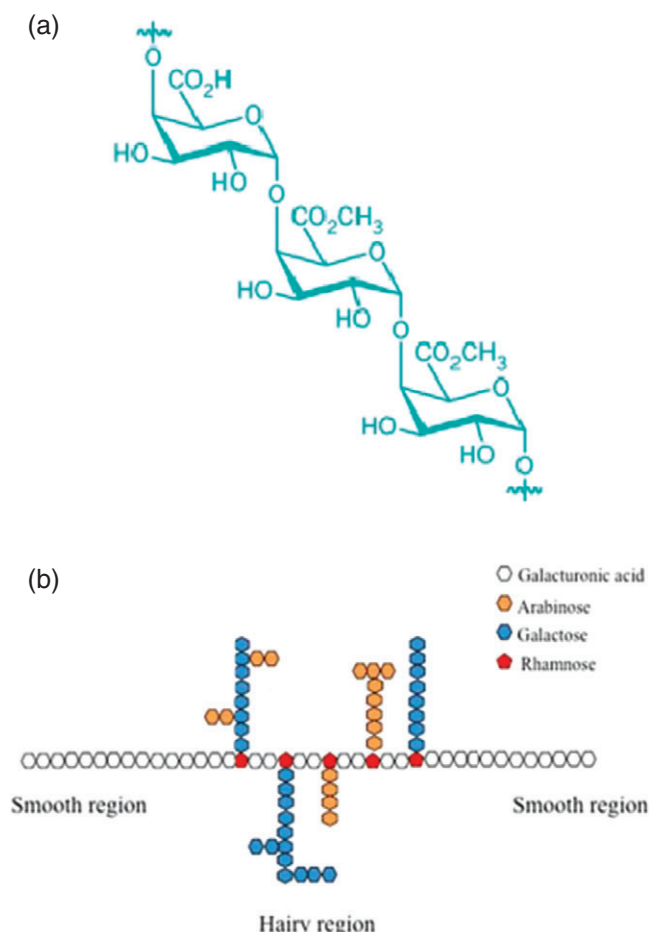


Figure 1. (a) The backbone of 1,4-linked α -D-galacturonic acid. The acid groups may either be free, combined as a methyl ester, or as sodium, potassium, calcium or magnesium salts. (b) Hairy and smooth regions of pectin. Selected regions of pectins: a backbone of 1,4-linked α -D-galacturonic acid, which represents the smooth region and contains a variable number of methyl ester groups and a hairy region consists of rhamnogalacturonan-I and rhamnogalacturonan-II, branched polysaccharides containing blocks of neutral monosaccharidic units, galactose, and rhamnose. (Reproduced with permission from Gentilini *et al.*².)

Production of pectin started in Germany in the early 1900s 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 a gelling agent. Demand was high, and in the 1930s the process was industrialized by new companies such as *Opetka*, *Obipektin*, and *Herbstreith & Fox* at new industrial sites established near apple-juice producers. The prolonged market success of this new product incidentally shows the industrial relevance of using a fruit by-product – until

then discarded as waste – as valuable raw material in the production of a valued natural product.

Today, pectin – mainly extracted from citrus peel – is a natural product of increasing importance knowing a constant growth in production and utilization.⁵

Excellent books¹ and reviews detail the biochemistry⁶ and the chemistry⁷ of pectin, including thorough reviews on its pharmaceutical uses,⁸ biomedical applications of pectin in various forms (polymer hydrogels, films, tablets, microspheres, nanoparticles and scaffolds) as novel biomaterial,⁹ as well as on the emerging use of pectin-based edible films incorporating natural antimicrobials for active food packaging.¹⁰

Chemical and biochemical research on pectin actively continues worldwide. Suffice it to mention here the exceptionally enhanced elasticity and mechanical strength of silk/pectin hydrogel, investigated as implantable bioscaffold material to regenerate cartilage and bone;¹¹ and the new method of treating chronic inflammation by intravenous administration of aqueous modified pectin solutions with molecular weights greater than 25 kilodaltons recently patented by a US pharmaceutical company.¹²

We provide an updated overview of pectin extraction and applications in the context of the biorefinery, namely the manufacturing unit of the emerging bioeconomy.¹³ The study identifies open opportunities toward larger scale production of this valued biopolymer, including efforts toward broadening the sourcing of raw materials and improving the extraction methods. Offering a unified view of the main research and utilization trends, the study is concluded by arguments supporting our viewpoint that pectin will shortly emerge as a central product of the biorefinery, and of the citrus-based biorefinery in particular.

Extraction and uses

Production

As already mentioned, today pectin is mostly produced from citrus peels and apple pomace, namely two by-products of fruit-juice production, with a minor fraction being obtained from sugarbeet (Fig. 2).

Prior to pectin extraction with dilute mineral acids, the citrus peel must be dried from the starting level of about 82% moisture, down to 10–12% moisture so as to avoid fermentation. Because of the high water content and the perishable nature of the waste, drying is economically viable only if close to the processing (orange juice) plant, and only where large amounts of waste accumulate.

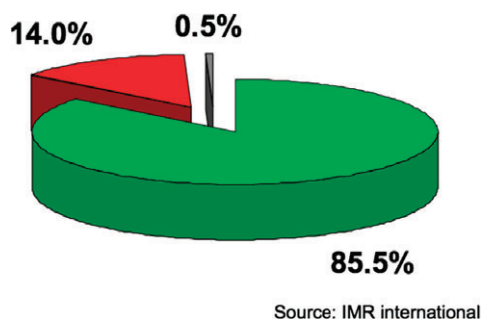


Figure 2. Raw materials used for pectin manufacturing as of 2009 (Lemon/Lime/Orange in green; apple in red, sugarbeet in grey). (Reproduced from Staunstrup¹⁴ with kind permission.)

In detail, after pressing the citrus fruit, the peel is dried at temperature that should not exceed 110°C.¹⁵ Rotary or direct fire dryers are normally used, avoiding direct contact between the flame and peel.

The high cost of the desiccation plant and process perhaps explains why so few plants exist in southern Europe (where citrus is mostly grown), while Argentina leads the export of dried citrus peel to main citrus pectin manufacturers worldwide.

Brazil and Mexico use orange and lime peel as the main pectin raw material (Fig. 3), while current production in China mainly relies on apple pomace. Independently of the raw material, however, the current manufacturing process is based on extraction via acid hydrolysis in hot

water. Careful processing is needed with regard to both the pH and hydrolysis time, as polymeric degradation can otherwise rapidly take place. In detail, manufacturers use a dilute mineral acid (HCl or HNO₃ or H₂SO₄) between 50°C and 100°C and at pH 2–3 for several hours to solubilize the protopectin.

Following separation, the pectin extract is filtered, concentrated, and precipitated with isopropyl alcohol. The alcohol is recovered by distillation while the pectin is washed and eventually dried.

When pectin is extracted, much of the ‘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. Common yields of pectin are ~ 3% of the peel weight.¹⁶ Eventually, out of a single lemon (200 g) affording the first 100 g of wet peel and then 13 g of dry peel, typically 3 g of pectin is obtained, and 10 g of depectinized peel goes to cattle feeding (Fig. 3).

The chemical characteristics of the extracted pectin depend on extraction conditions, and the sourcing material. Hence, prior to shipping, the product obtained is characterized (pectin for use in food is a polymer with at least 65% galacturonic acid units), and separated into low and high methoxyl pectin (LM and HM) with degree of esterification (DE) >50% and <50%, respectively (Table 1).

The DE value determines the degree of reactivity with calcium and other cations. Optionally, further de-esterification

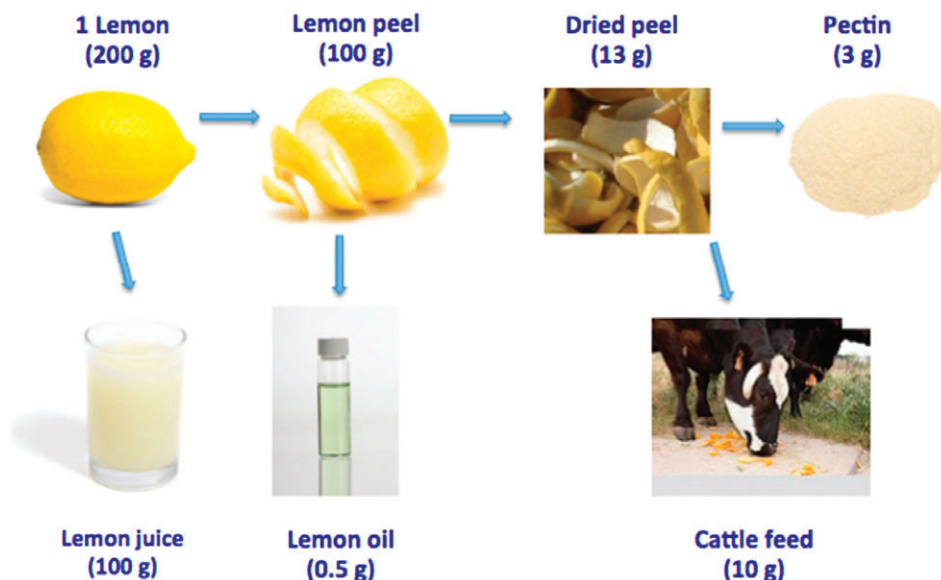


Figure 3. Pectin is extracted from dried lemon peel, after extraction of d-limonene. The remainder material is sold as excellent cattle feed with many beneficial properties. (Adapted from Staunstrup¹⁴ with kind permission.)

Table 1. The three groups of pectins classified on the basis of their different gelling properties.

<p>High methoxyl pectins (HM pectins)</p> <p>These pectins have usually a more than 50% share of esterified polygalacturonic acid units (DE). Almost no reaction with calcium ions occurs, while gel forms at high sugar concentration or low pH. HM pectin is further commercialized as:</p> <ul style="list-style-type: none"> • Rapid set pectin • Medium rapid set pectin • Slow set pectin • Buffer pectin • Calcium sensitive pectin
<p>Low methoxyl pectins (LM pectins)</p> <p>Pectins with DE < 50%. Besides with sugar and acids, LM pectins gelify with calcium ions at low concentration and at a high pH-value, opening numerous application possibilities in dietetic and dairy products. LM pectin is further commercialized as:</p> <ul style="list-style-type: none"> • High calcium sensitive LM pectin • Low calcium sensitive LM pectin
<p>Amidated pectins (HM and LM amidated pectins)</p> <p>In case of amidated pectins ammonia is used for de-esterification. Part of the ester groups is then replaced by amide groups. This process modifies the gelling properties in comparison to acid de-esterified pectins.</p>

of the high methylester pectin with acid or alkali, or amidation is carried out with ammonia to form amidated pectins which, when compared to LM pectins, need less calcium to gel, and are less sensitive to precipitation by high amounts of calcium.¹⁷

Selected companies extracting pectin and commercializing it worldwide include *CP Kelco* (in Denmark and Brazil), *Ceamsa* (in Spain), *Yantal Andre Pectin* (in China), *FMC Specialty Chemicals* (USA), *Du Pont Danisco* (in the USA and Mexico), *Herbstreith & Fox* (in Germany), *Naturex* (production units in France, the USA, and Poland), *Cargill Texturizing Solutions* (in Belgium), *Nexira* (France) and *Taiyo Kagaku* (Japan), and *B&V and Silvaextracts* (in Italy).

Gel-forming properties

The gel-forming ability of pectin that gives pectin its name is due to the ease of association of pectin chains in water, leading to the formation of three-dimensional network comprised of long segments of galacturonic acid moieties, interrupted by the incorporation of rhamnose and branching of the chain. Two or more chain segments bond together and start to interact. In general, the high content of galacturonic acid and the low degree of methyl

esterification promote the availability of COO⁻ groups, involved in the gelling process.¹⁸

HM pectins gel predominantly in the ‘sugar-acid gelling mechanism’,¹⁹ for which a certain amount of acid is required to suppress the dissociation of the free carboxyl groups, thereby preventing repulsion of negatively charged moieties. At high sugar concentration, the pectin molecules are dehydrated promoting chain-chain rather than chain-solvent interaction.

LM pectins, too, are able to form gels in a sugar-acid gelling mechanism. Pectin molecules with a low ester content, however, may form gels in a broad pH range in the presence of multivalent cations (e.g. Ca²⁺ ions). The calcium concentration required for gelling depends on pH and soluble solids. With relatively small additions of calcium, a gel will form. Over dosage of calcium ions will lead to irreversible calcium pectinate precipitation.

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,²⁰ 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 pectins additionally provides advantages regarding protein stabilization in acidified milk drinks.

Uses

Pectin is widely approved worldwide for use in foods as a safe additive (pectin has the GRAS status and in Europe, it is an approved food additive coded *E440a* (for low and high methoxyl pectin) or *E440b* (for amidated pectins). Being an indigestible soluble fiber, its content is restricted between 0.5% and 1.0%. Consumers worldwide appreciate its natural origin in fruit and since a decade, its consumption is growing at fast (ca. 10%) annual growth rate.

Traditionally, pectin was primarily used in the production of jams and fruit jellies, and in products with high sugar content, wherein pectin secures the desired texture, limits the creation of water/juice on the surface, and ensures an even distribution of fruit in the product. In detail, high-density pectin is used by the confectionery industry; while medium- and low-density pectin is used for the production of yogurt and fruit juice. In the last decade, pectin’s thickening and stabilizing attributes have made it an essential additive in the production of yogurts and fruit juices in which pectin is also increasingly used to stabilize acidic proteins.

In 1991, a large chemical company introduced liquid extract of citrus pectin (tradenamed *Slendid*) as a new fat replacer in a variety of processed foods.²¹

Twenty-five years later, pectin is widely used as a sugar and fat substitute in several food products thanks to its mouthfeel mimicking sugar and texture mimicking fat, where this natural hydrocolloid allows recovery of the mouthfeel lost when removing sugar and fat. In low-fat yogurts in which the protein content is lower due to the use of skim milk, for example, pectin is used for both stability and mouthfeel development.

Being a bioactive hydrocolloid with an excellent safety profile, pectin is also being increasingly used in cosmetics and in medicine. In cosmetics and in personal care products, besides use as natural texture for ointments, oils, and creams, and as an effective thickener and stabilizer for shampoos, lotions, and hair tonics. Pectin is now also used as an effective skin anti-aging agent.²²

In medicine, pectin is used in wound-healing preparations and in specialty medicine adhesives like colostomy devices. Pectin is a natural part of the human diet, and its intake is highly beneficial; pectin binds to cholesterol in the gastrointestinal tract (reducing blood cholesterol levels), and slows glucose absorption by trapping carbohydrates.²³

Numerous drugs are encapsulated with a pectin film to protect the gastric mucosa and to allow sustained release of the active ingredient into blood.²⁴ As already mentioned, intravenous administration of aqueous modified pectin solutions (GCS-100, a complex polysaccharide derived from pectin with molecular weights greater than 25 kDa) is now in phase III in the USA as a new method of treating chronic inflammation (GCS-100, a complex polysaccharide derived from pectin that binds to, and blocks the activity of, galectin-3, a type of galectin whose over-expression has been implicated in a number of serious human diseases).¹²

Market

Global demand for functional foods has been constantly rising for two decades, translating into an expanded market for hydrocolloids,²⁵ including pectin, which is the most label- and consumer-friendly of all hydrocolloids. Pectin, however, is increasingly used also by the cosmetic and pharmaceutical industries. In 2010, the average price was \$14.30/kg, and the global market was valued \$656 million.²³ The same market analyst was forecasting 5.4% annual growth rate to reach \$856 million in 2015.²³

In subsequent few years, however, market growth has been considerably faster. In 2013, a leading chemical

magazine reported that the global pectin market had reached \$850 million.²⁶

It is informative, here, to compare these figures with those forecasted in 2009 by an industry's practitioner at a leading pectin's manufacturer.¹⁴ The market was then quantified at 30 000 tonnes, with prices of HM and LM comprised between 11\$ and 12.9\$ per kilogram (Table 2), which would translate into a \$340 million market.

Yet, as already mentioned, the current pectin's market exceeds \$850 million and global output exceeds 40 000 tonnes,⁵ with independent market analysis⁵ pointing to >5% annual growth for each of the main market segments (fruit spreads and fillings, dairy, confectionary, beverages, and other).

Despite the technical ease of the extraction process, and the abundance of raw biomaterials, the pectin market has been for decades heavily consolidated. A map showing the sites of global manufacturers in 2009 is revealing (Fig. 4). Only one producer was based in China, one each in Brazil and in Mexico, and most of manufacturers located in Europe, where production of pectin started about one century ago.

Pointing to increasing competition and production levels, however, since then several new companies have entered the market, including both new manufacturers producing relatively low volumes mainly serving domestic markets, and large specialty chemicals makers. The independent market report mentioned above,⁵ for example, mentions 24 major (global) producers, and several other minor manufacturers.

In 2013, the top five exporters were Germany, (with exports valued at >\$430 million), followed by Mexico (\$160 million), Brazil (\$70 million), Czech Republic and China (ca. \$50 million) each.²⁷ Remarkably Germany was also the second biggest importer, preceded only by the USA. Japan, France and Russia are all net importers (Fig. 5).

The waste orange peel biorefinery

A truly economically and environmentally sustainable biorefinery¹³ preferentially uses green chemistry processes

Table 2. The pectin market in 2009 (Adapted from Staunstrup¹⁵ with kind permission).

Market	Growth rate		Current price		
	LM pectin	Overall LM pectin	HM	LM	
30 000 tonnes	~5000 tonnes	6%	10–20%	\$11.00/kg	\$12.90/kg

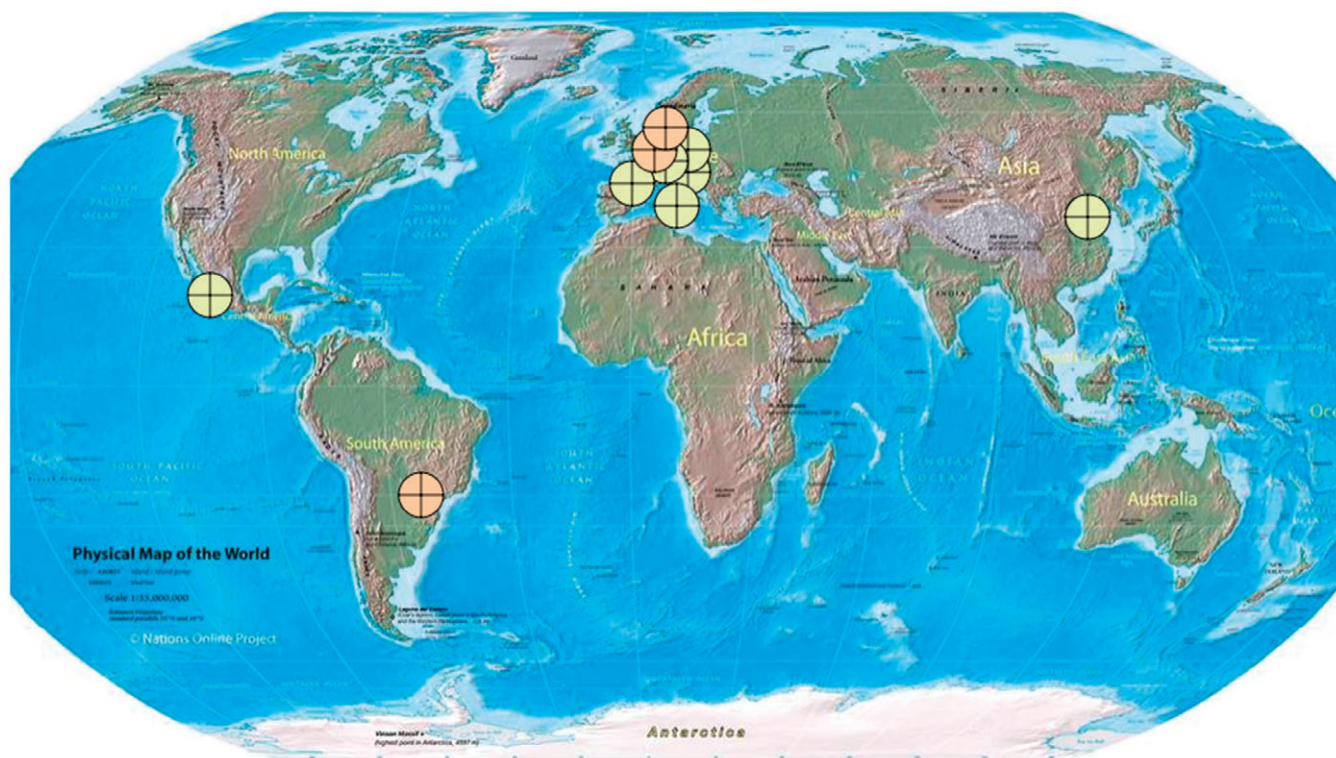
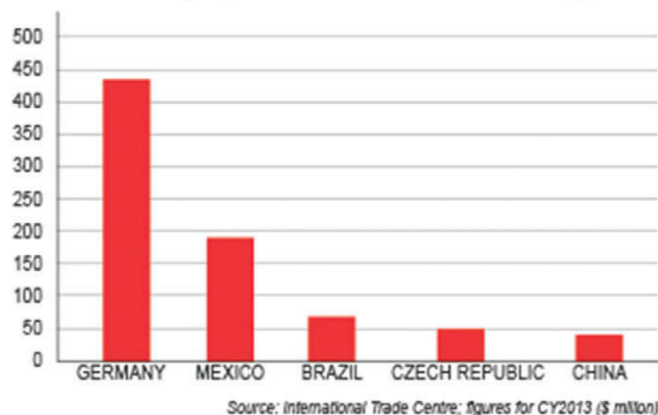


Figure 4. World’s distribution of pectin manufacturing plants, as of 2009. (Reproduced from Staunstrup¹⁴ with kind permission).

Top pectin exporters

In 2013, Germany exported over \$430 million worth of pectin



Top pectin importers

USA was the biggest pectin importer in the world in 2013

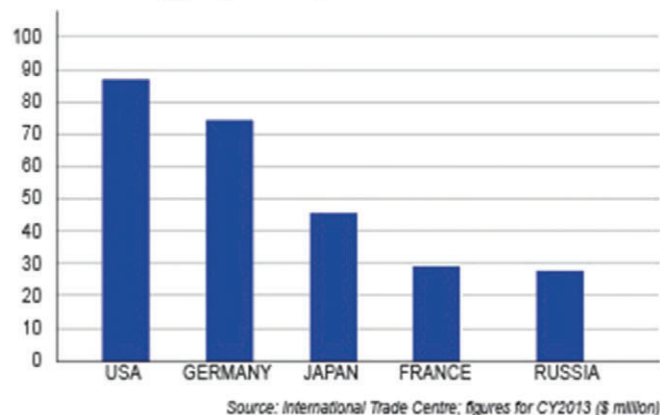


Figure 5. The USA with imports valued at \$90 million, Germany (\$75 million), Japan (\$45 million), France (\$29 million) and Russia (\$27 million) were the major importers of pectin during 2013. (Reproduced from Menon²⁷ with kind permission.)

to convert biomass generated as residues (former ‘waste’) of agricultural and related food industry activities into high value-added chemical products. Numerous different biorefineries using food waste will shortly emerge as the central manufacturing units of a more sustainable society based on a bioeconomy.²⁸ Clark *et al.* in the UK

were amongst the first to investigate and demonstrate in 2012 the economic and technical feasibility of the waste orange peel biorefinery using clean microwave-based technology.²⁹ Here, a brief insight of India’s lack of domestic pectin shows the opportunity to invest in similar citrus biorefineries where to produce pectin.

With over 5 million tonnes per year, India ranks fourth among top orange-producing countries.³⁰ Yet, domestic production of pectin is largely insufficient to meet the rapidly growing demand. India's pectin imports almost tripled from \$4.84 million in 2012 to \$10.14 million in 2014 (over 1000 tonnes imported).²⁷ Most pectin originates from Brazil (citrus pectin) and from China (apple pectin) where pectin makers are capable of supplying the large quantities required by food companies, at around \$10 per kilogram.²⁷

Investing in domestic plants would enable India's pectin manufacturers to meet the burgeoning demand, cutting through the cost of transport and custom duties (>15%) on imported pectin. Starting to extract pectin would create a new industry, at the same time reducing the environmental impact of the citrus industry by reusing what is still now considered waste. Similar arguments hold their validity for many citrus-making countries.

New raw materials and new extraction methods

Facing a rapidly growing market, research institutes based in large countries where abundant amounts of fruit by-products are available, are currently investigating ways to extract pectin from other fruit waste, beyond or along with citrus peel and apple pomace. Pectin, indeed, is abundant in many different sources of vegetative origin, including coffee beans, prickly pears and sunflower seeds (Table 3).

Sugarbeet pectin has already found a niche market due to its unusual emulsification properties (this pectin hardly gels, but it is an excellent emulsifier).³¹ Other sources of pectin are beginning to find markets, such as sunflower pectin.

The excellent rheological behavior of pectin obtained from sunflower heads,³² indeed, supports its extraction from this abundant agriculture by-product which is already used for commercial production of pectin, for example in India by *Krishna Pectins*.³³

Table 3. The amounts of pectin from different sources (% in dry fruit). (Reproduced from Braconnot² with kind permission).

Apple pomace: 10–15%
Citrus peel: 25–35%
Sugarbeet: 10–20%
Sunflower: 15–25%

Scientists in Colombia have lately advanced the extraction of pectin from the residues of the coffee beans used to produce coffee, aiming at forthcoming production.³⁵ Previously, a team in Mexico showed that chickpea husk is an excellent source of LM pectin of high molecular weight.³⁵

Another research team in Mexico, the world's largest producer of *Opuntia* plants, found that the peel of prickly pear fruit affords high-molecular-weight pectins ($M_w = 10.16 \times 10^5 \text{ g mol}^{-1}$, $M_n = 9.10 \times 10^5 \text{ g mol}^{-1}$), which contain 65.4 % galacturonic acid with a degree of esterification of 30.7%.³⁶ Their aqueous solutions (0.5 to 2%) showed high viscosities and shear thinning behavior, even higher than those of some commercial citrus pectins. Moreover, the low degree of esterification of the prickly pear pectin yielded a high calcium reactivity which led to the formation of soft and elastic gels.

For at least a decade, it is known that extraction employing microwave (rather than thermal) heating is generally a much more effective method of extracting pectin from citrus peel, affording a product with better quality in higher yield and in considerably shorter times.³⁷ Maximum pectin yield (5.27% on a dry basis for 15 min of extraction) is obtained under strongly acidic (pH = 1.5) conditions.³⁸

In 2012, Clark *et al.* further advanced the microwave-based method by developing a green, one-step process that efficiently and simultaneously extracts compounds in the orange peels via exposure to high-intensity microwaves at room temperature in the absence of acids, transforming many components of the orange peel into liquid that can be then easily separated into useful products.³⁹

The solid remainder is mesoporous cellulose, which can be used as a food additive, thickening agent or eco-friendly adsorbent. The process is optimally run by adding a relatively low amount of water (e.g. 40 g of peel in 20 mL of water) under microwave irradiation (800 W).²⁹

Previously Kratchanov *et al.* in Bulgaria demonstrated that by combining ultrasound irradiation of apple pomace with acid maceration affords higher yields of high-quality pectin when compared to conventional hydrolytic extraction.⁴⁰

More recently, a research team in Italy has shown that extraction of pectin from *Aloe vera* previously irradiated with microwaves and further extracted using sodium citrate in place of HCl (pH 7.6 of sodium citrate solution compared to pH 2.9 of hydrogen chloride solution), leads to complete extraction of pectin of high molecular weight and ultralow DE (2.93%).² The resulting gel formed by addition of Ca^{2+} has distinctly improved cytocompatibility compared to commercial LM pectin.

Perspectives and conclusions

Pectin, the partial methyl esters of polygalacturonic acid and its salt obtained by extraction in an aqueous medium, is an exceptional polymer whose large and increasing use as hydrocolloid by the food industry is rapidly expanding into other industrial sectors. Even in the food sector, traditional usage as a thickening and stabilizing agent is being complemented by the emerging utilization of pectin as a fat replacer, while producing improved texture.⁴¹

Novel biomaterials for regenerative medicine,^{1,2} and powerful anti-inflammatory drugs,¹² are just some of the advanced applications of this unique biopolymer that will likely (and shortly) have a huge impact on medicine.

The need to expand its production and renew conventional extraction methods meets the emergence of novel citrus-biorefineries in citrus-making countries, where the citrus fruit production has grown from 78 million tonnes in 1990 to 123 million tonnes between in 2010 (and has, ever since, continued to grow).⁴²

In 2013, Clark *et al.* conducted an economic investigation of the economics of the microwave, acid-free extraction process assuming to process 50 000 tonnes of orange peel, and selling pectin at £11 per kg and *d*-limonene at £ 0.62 per kg.⁴³ The latter figure was wrong, because *d*-limonene currently sells at \$14 per kg, and even in 2013 it was sold at \$10/kg. In any case, the high materials efficiency of the microwave-based process would afford (from 50 000 tonnes of wet orange peel) 152 tonnes of *d*-limonene and 1080 metric tonnes of pectin per year.

Using current market value figures for both limonene and pectin (\$14/kg and \$10/kg, respectively), revenues from pectin sales would amount to 83% of the overall revenue (\$10.8 million for pectin and \$2.128 million from *d*-limonene), hence demonstrating the central role of this biopolymer for any citrus-based biorefinery yet to come.

In conclusion, new extraction methods, replacing obsolete hydrolysis of protopectin in hot water with dilute mineral acids, have been developed. The new methods are clean, economically viable, and can be applied to process different pectin sources, eventually affording plenty of HM and LM pectins to meet the current and forthcoming demand. This will feed back into increased supply and eventually lead to lower prices and larger utilization across many different commercial sectors. Providing a unified overview of this important domain of today's chemical research, this study will contribute toward the emergence of numerous citrus-based biorefineries worldwide.

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