PECTIN

Introduction

The word ‘pectin’ derived from Greek, it means ‘congealed (semi solid). It has been recognized for at least 200 years and was originally identified in 1790 in apples by the French chemist Nicholas Vauquelin (who also discovered the elements chromium and beryllium). Until 1984 there were no further reports available on pectins and later the scientist, Braconnot was undertaken. He has named the acid, gelling substance pectic acid after the Greek word for gelling or congealing. Further, Smolenski identified the gelling substance as a polymer of galacturonic acid and later on in the 1937 Schneider and Bock established the basic formula of pectin.

Pectin’s are the mixtures of polysaccharides, which is found as a major component of cell walls in all plants particularly apples or citrus fruits. Pectin’s are complex heteropolysaccharide composed primarily of essentially linear polymers of α-D-galactopyranosyluronic acid units linked through $\alpha-\Delta = (1-> 4)$ glycosidic linkages; the polymer chains are esterified to various degrees with methanol. This regular structure is interrupted, however, with L-rhamnopyranosyl units and with side chains containing other neutral sugars. The polymer chains may also be partially acetylated. The most important physical property of pectin is its ability to form spreadable gels. Gel formation results when the polymer chains interact over a portion of their length to form a three-dimensional network. This aggregation of chains occurs through hydrogen bonding, divalent cation cross bridging, and/or hydrophobic interactions. Pectin contains pectinic acids as major components, water soluble, and able to form gels under appropriate conditions.

In this episode the following five divisions have been studied on pectins.

1. **Sources of Pectins**
2. **Properties of Pectins**
3. **Classification of Pectins**
4. **Extraction of Pectins**
5. **Application of Pectins**

1. SOURCES OF PECTINS:

Presently, the traditional, commercial sources of pectin have been majorly extracted from citrus peel and apple pomace, which are by-products of juice manufacturing units.

Citrus peel, generally lemon and lime peel are one of the most preferred sources for the manufacture of pectin due to its high pectin content and good colour properties. Pectin can converts to pectic acid upon the hydrolysis of lime treated peel and further treated with enzyme to ease the peel removal. Apple pomace contains 10-15% of pectin's, whereas citrus peel contains relatively higher i.e., 20-30% of pectin's. More recently other sources of pectins are beginning to search for market include sugar beet waste from sugar manufacturing, sunflower heads (seeds used for edible oil), and mango waste. Also, crab-apples, gooseberries, some type of plums, high bush cranberries, strawberries, cherries, blueberries and papaya contains little percentage of pectin's.

2. PROPERTIES OF PECTINS:

The gelation property of pectins can be divided into two main categories: high methoxy gelation and low methoxy gelation. High methoxy gelation pectin usually forms at a pH of below 3.5 and total solids content of above 55%. This type of gel formed during jam making and high methoxy pectins are characterised by their setting time and the gel strength. Setting time is usually categorized as rapid set, medium set and slow set. High methoxy pectins gel slower as more of the methoxy groups are removed during processing.

Low methoxy pectin is gelled with calcium ions and hence is not dependant on the presence of acid or high solids content. The low methoxy pectin has the lowest level of esterification and amidation can interfere with the gelation causing the gelation to be delayed. Another useful property of amidated pectins is the ability of the gel to reheal after shearing.

Monovalent cation salts of pectinic and pectic acids are usually soluble in water; di- and trivalent cations salts are weakly soluble or insoluble. Dry powdered pectin, when added to water, has a tendency to hydrate very rapidly, forming clumps. These clumps consist of semidry packets of pectin contained in an envelope of highly hydrated outer coating. Clump formation can be prevented by dry mixing pectin powder with water-soluble carrier material or by the use of pectin having improved dispersibility through special treatment during manufacturing.

CHEMICAL STRUCTURE AND COMPOSITION OF PECTINS:

The composition and chemical structures of the elements that constitute pectin depend on environmental conditions, and plant source. In addition, pectin structure is modified by enzymatic and chemical reactions during plant growth, fruit ripening, and extraction techniques or conditions. All of the above factors make the structure and molecular weight of pectin to vary from plants to plants and even among tissues in the same plants. Therefore, Chemical structure and composition of pectin's are studied by classifying them into Native and commercial pectins.

NATIVE PECTINS:

Native pectin is composed of three major polysaccharides, all containing α (1→4)-D-galacturonic acid residues; usually referred as galacturonans. These are homogalacturonan, rhamnogalacturonan-I, and rhamnogalacturonan-II. (**Fig. 1**)

Homogalacturonan is a linear chain of α (1→4)-D-galacturonic acid residue with a variable degree of methyl esterification at the carboxyl group. It could be *O*-acetylated at C-2 or C-3 depending on the source

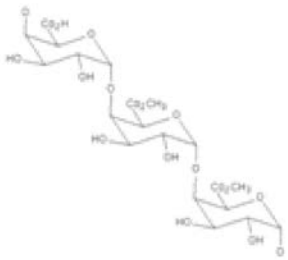
Rhamnogalacturonan-I consists of repeating units of the disaccharide α (1→2)-L-rhamnose-α (1→4)-D-galacturonic acid. Galacturonic acid residues can be *O*-acetylated at the C-2 or C-3, while 20-80% of the rhamnose residues can be substituted at C-4 or C-3 with neutral sugar side chains. The composition of the neutral sugars varies among plant sources as D-galactose, L-arabinose, and D-xylose being the most common. Other neutral sugars such as D-glucose, D-mannose, L-fucose, and D-glucuronic acid are found less frequently.

Rhamnogalacturonan-II, represents its misleading identification, has a backbone of α (1→4)-D-galacturonic acid. Some of the side chains attached to the backbone have been identified as 2-keto-3-deoxy-D-manno-octulosonic acid, 3-deoxy-D-lyxo-2- heptulosaric acid, apiose, and aceric acid. All neutral sugars are located in side chains are rhamnogalacturonan I and II domains, and therefore, these domains are often referred as “hairy regions”.

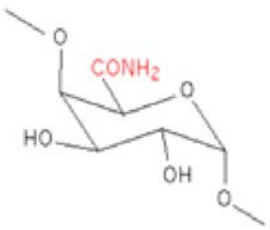
In addition to the above three major domains, arabinogalactans, arabinans, and xylogalacturonans are also found in native pectin, all lacking the galacturonan backbone.

COMMERCIAL PECTINS:

Commercial pectins are structurally less complex due to the industrial extraction and purification process, which remove most of the neutral sugars. These consist mainly, a backbone of α (1→4)-D-galacturonic acid with partial methyl esterification of the carboxyl groups (May 1990). At least 65% of the extracted material must be galacturonic acid, in order for extracted material to be classified as commercial pectin



Pectin



Amidated pectin

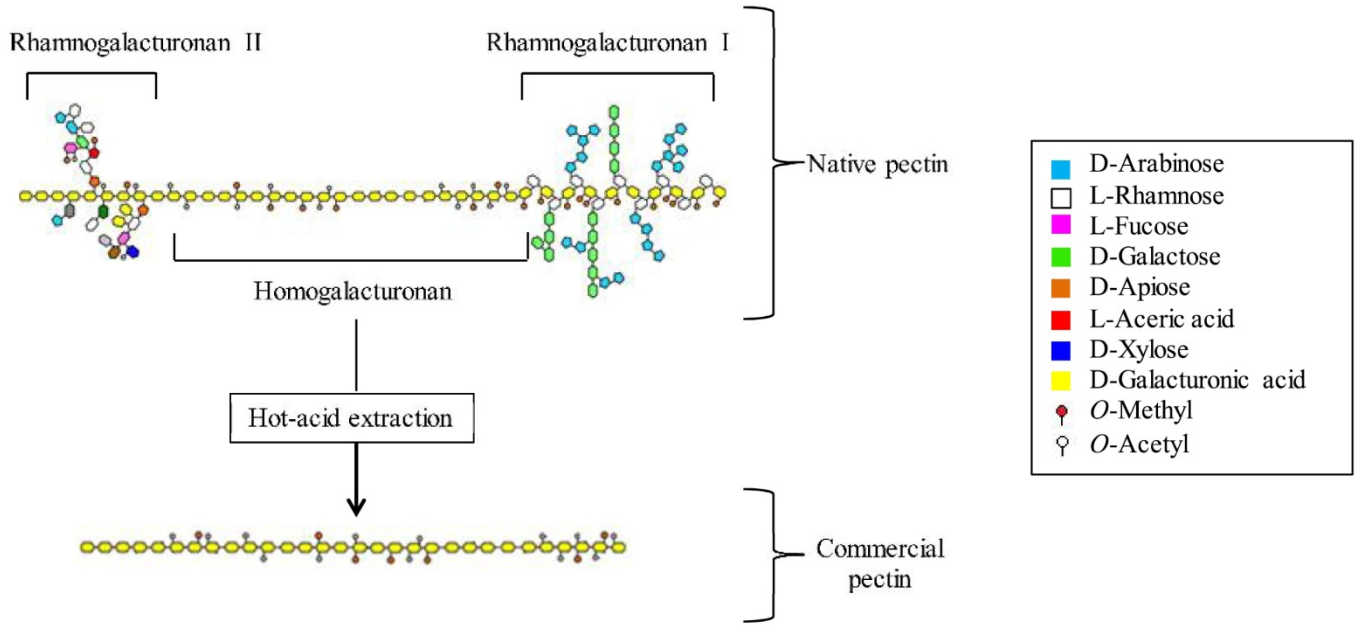


Fig. 1: Schematic structure of native and commercial pectin

3. CLASSIFICATION OF PECTINS:

Pectin's are subdivided according to their degree of esterification (DE), a designation of the percent of carboxyl groups esterified with methanol. Pectin's with DE > 50 are high-methoxyl pectins (HM-pectins); those with DE < 50% are low-methoxyl pectins (LM-pectins).

The degree of amidation (DA) indicates the percent of carboxyl groups in the amide form

- Rapid Set pectin is a high-methoxyl form of the substance, meaning it contains high quantities of the compound CH_3O. It is most often used in preserves that contain bits of fruit or vegetable, such as jams and marmalades.
- Slow set pectin, another high-methoxyl form of pectin, is used in less pulp-laden jellies, such as apricot and grape jelly. It's also used in some less pulpy jams and preserves.
- Stabilizing pectins are most commonly used in dairy products. Specifically, they are used to stabilize acidic proteins in dairy products during any heat processing used to manufacture the product. Stabilizing pectins can be found in yogurt, soya beverages and whey beverages.

- Low methoxyl pectin, also known as LM pectin, is often used for products with reduced sugar content. This form of pectin needs calcium as a catalyst to begin the gelling process. Products containing LM pectin include reduced sugar preserves, sauces, marinades and dessert toppings. LM pectin is also used in low acid fruit preserves, such as fig preserves.

4. EXTRACTION OF PECTINS:

The processing of apple fruits for juice and cider making results in large amounts of solid byproducts, which are termed “apple pomace”. Apple pomace approximately accounts 25- 35% (w/w) of the fresh apple fruits that are processed. Apple pomace is mainly composed of carbohydrates, fibers, proteins, and small quantities of minerals and considered a rich source of dietary fiber, especially pectin with 10-15% content (w/w dry basis).

The feasibility of the processing operations of pectin production and its wide use in various applications make pectin extraction an effective way to utilize apple pomace. Pectin production is sometimes considered an art rather than a science because a little vary in the experimental parameters such as Temperature, p^H, time etc. will vary the pectin characteristics such as molecular weight, degree of esterification, yield, etc.

Pectin extraction is a multi-stage physicochemical process, where pectin molecules are hydrolyzed and solubilized from the cell wall and middle lamella of the plant tissue. Extraction conditions used in the process vary depending upon the raw material, desired type of pectin, and process economics. Commercial pectin is usually produced by hot acid extraction, followed by filtration, alcohol precipitation, drying, grinding, and standardization and schematically represented in **Fig. 2.**

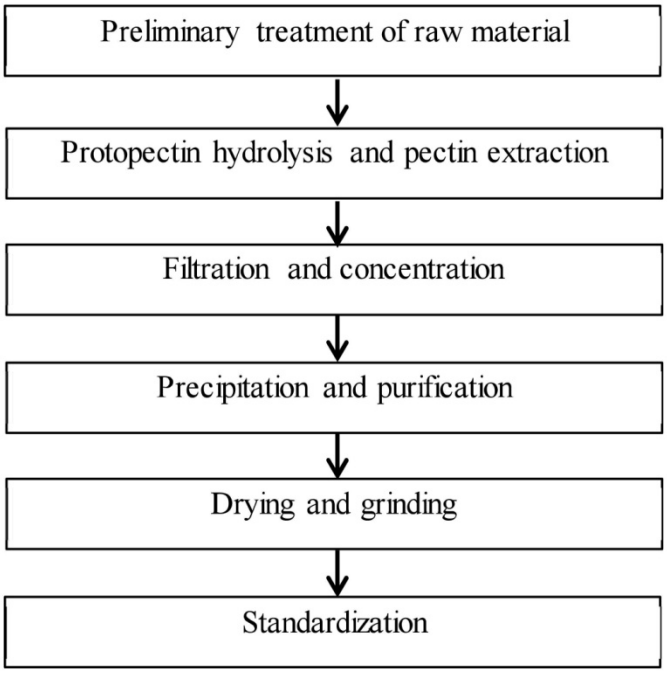


Fig. 2. Schematic diagram of Pectin

Apple pomace was blended with distilled water for one minute using a laboratory blender at high speed. The slurry was transferred to a glass beaker and distilled water were added and heated under continuous stirring using a digital hot plate stirrer with a thermostat control until 20°C was reached. Hydrochloric acid was added to set the pH to 1.5, 2.5, or 3.5; pH was monitored using pH meter equipped with a temperature compensation probe. Dispersions were heated at the specific extraction temperature under continuous stirring (350 rpm) using a digital hot plate stirrer.

The slurry was cooled to room temperature, using an ice bath. Then separate the liquid portion and the slurry was centrifuged. The supernatants were filtered through a Buncher funnel with a Whatman No.4 filter paper. The pH of filtrated supernatants was adjusted to 3.5 with 1M sodium hydroxide. Then the extract was mixed with an equal volume of ethanol, and stirred for 10 minutes at room temperature. The precipitate was separated from alcohol by centrifugation. Then the precipitate was dispersed in 500ml of 70% ethanol and stirred for 10 minutes at room temperature, and the alcohol was removed by centrifugation. The extracted pectin was freeze dried under -50°C and 0.22 mbar by a bench top freeze drying for approximately 60h. The dried pectin grind into a fine powder.

5. APPLICATIONS:

Depending on the chemical characteristics of pectin, it is used in numerous food applications as a gelling agent, thickener, stabilizer, and emulsifier.

The traditional application of pectin is as a gelling agent in a wide range of fruit-based products like jams, marmalades, jellies, fruit preparations for yoghurts and desserts and fruit filling for bakery products. It can be used to improve the mouth-feel and the pulp stability in juice based drinks and as a stabilizer in acidic protein beverages. And also reduces syneresis in jams and marmalades and increases the gel strength of low calorie jams.

Besides its use in the food industry, over the past few decades' pectin is also used in pharmaceutical and cosmetic products**.** Various properties of pectin, such as gelling, emulsifying, and film forming abilities, in addition to its resistance to degradation in the upper gastro intestinal tract, has allowed the increasing use of pectin in the development of drug delivery systems through encapsulation.

FOOD

Pectin has the potential to be used in the encapsulation of unstable food ingredients such as

1. High methylated pectin's are used in jams and jellies. The role of the pectin is to impart a gel texture to the jam or jelly. This texture must be strong enough to allow transportation and storage without changes. It is mainly used for fruit flavored products, where the acidity enhances most fruit flavors. The pectin is used within the confectionery industry for making fruit jellies, jelly centre's, and wine gums. In wine gum formulations it is often combined with gelatin. It is also used for aerated products together with whipping agents.
2. Stabilization of protein containing drinks with pH around 4 is an increasingly an important application area for pectin. Types of drinks like yoghurt drinks, milk-juice drinks, acidified whey drinks, and acidified soy drinks.
3. Pectin is used for fat replacement in low-fat spreads and butter spreads. In these products, it binds water and thereby improves the emulsion stability. A pectin type, SLENDID®, has been developed to mimic a fat-like mouth feel.

4. Pectin is used in fruit-milk desserts, where the interaction with calcium is utilized to obtain an instant gelation when adding calcium ions (milk) to syrup containing pectin. In milk desserts, LMA pectin is incorporated to provide texture and mouth feel, often in combination with other stabilizers
5. α-tocopherol, which is the most abundant and active form of vitamin E, is commonly used by the food industry for food fortification and to inhibit lipid oxidation. However, the use of α-tocopherol is, sometimes, hindered by its sensitivity to heat, oxygen, and light, and high hydrophobicity. So, pectin could be used as an ingredient in the development of a polymeric matrix for the encapsulation of α-tocopherol, to provide protection, enhance the stability, and to deliver α-tocopherol under specific conditions, or gastrointestinal environments.

PHAMACEUTICAL/COSMETIC

1. Pectin has multiple beneficial effects on human health including lowering of blood cholesterol and serum glucose levels and the potential inhibition of cancer growth and metastasis. Some of these benefits may occur via the induction of apoptosis (programmed cell death) and/or the interfering with ligand: receptor interactions
2. Irritable bowel syndrome, a functional gastrointestinal disorder can be reduced by fiber diet means through pectin. In fact, one of the leading medications for this problem, Kaopectate®, used pectin as one its main “active” ingredients. Here Pectin acts as thickening agent and also found in other medicines such as Luden’s® (Cough syrups).
3. Orange peel pectin shows good potency as a binding agent.
4. The properties of pectin are utilized in a variety of personal care applications, including skin- and hair-care products and color cosmetics. Apart from providing structure in formulated products, pectin can form a gel on the skin.
5. The viscosity of pectin solutions is utilized to evenly distribute and provide non-slimy spreadability of hair conditioners and hair styling products.

Conclusions

In conclusion, Pectin is polysaccharides, which are localized in the primary cell wall and middle lamella in all higher plants. Pectin’s are responsible for different physiological processes like as

one of the main agents cementing the cellulose fibrils and may be linked covalently to other polymers. Commercial pectins are extracted at low pH and high temperature. Pectins are widely used as food additives with gelling and stabilizing properties in jams, jellies, milks and confectionery products. Pectins can be categorised according to their degree of esterification (DE), a designation of the percent of carboxyl groups esterified with methanol. Pectin's with DE > 50 are high-methoxyl pectins (HM-pectins); those with DE < 50% are low-methoxyl pectins (LM-pectins). The extraction of pectin is a multi-stage physicochemical process by hydrolyzed and solubilized from the cell wall and middle lamella of the plant tissue. The condition used for the extraction process varies depending upon the raw material, desired type of pectin, and process economics.