Technical Article

Introduction to Agar

Introduction

Agar, also known as agar-agar, is a cell wall polysaccharide that is extracted from certain red seaweeds and used as a gelling agent. The gelling fraction is essentially a sulphated galactan consisting of alternating units of α-(1-4)-L-galactose and β-(1-3)-D-galactopyranose. Agar has been widely used in the East for several hundred years, certainly since the seventeenth century when it is claimed to have been discovered in Japan by Tarazaemon Minoya (1658).

The industry as we know it today was founded on extraction from *Gelidium* seaweeds that were essentially wild harvested but with demand far out stripping natural supply, it now relies heavily on cultivated seaweeds, primarily species of *Gracilaria.* Other species used for the extraction of agar include *Gelidiella, Pterocladia & Ahnfeltia.* These different species yield agars with different properties.

← *Gelidium* seaweed, a source of agar

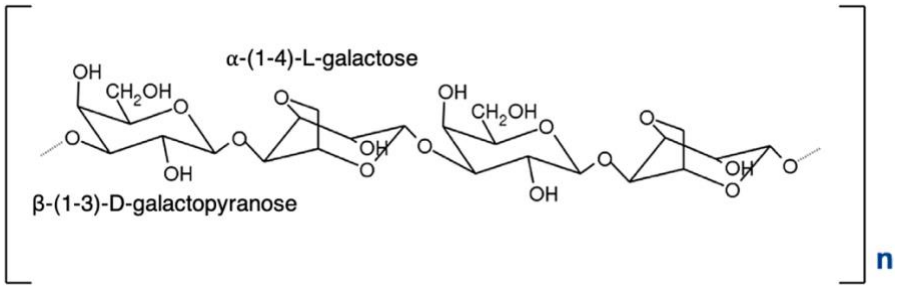
Agar is eaten extensively in Asia as a flavoured jelly where the brittle texture is appreciated. However, for western consumers brought up on the jelly texture of gelatin, this is less acceptable. Agar is useful in the food industry as a gelling and thickening agent with particularly good functionality in acidic dairy products where it is used as a stabiliser. Another key property of agar is the large hysteresis between the melting and setting temperatures which is unusual for a polysaccharide. One of the single biggest users of agar in the west is in the baking industry where the very high melting points of the agar gels make them particularly suitable to the baking process. Agar has good compatibility with sugar and can be used in very high sugar environments that would precipitate most other gums. Agar is often used to provide structure to high sugar systems such as doughnut icing.

Structure

The original structure of agar was believed to be a simple sulphated poly galactose, but it is actually a very complex polysaccharide that varies considerably in structure, depending on the source. Early work in 1930s showed that agar consisted of at least two separate polymers that could be fractionated - these being agarose and agaropectin. Later work has shown that the structure varies substantially across different raw materials, with species, environmental conditions and time of the year.

Agarose is the major component of agar and is the gelling fraction. It comprises repeating units of agarobiose which itself comprises alternating units of α-(1-4)-L-galactose and β-(1-3)-D-galactopyranose with varying amounts of sulphate, pyruvate, uronate and methoxyl groups present. The α-(1-4) residues can also be modified by the presence of a 3,6 anhydro bridges. The presence of anhydro bridges has a significant impact on the gelling functionality and varies across raw material sources. Modern alkali treatment methods can be used to increase the level of anhydro bridging in the molecule and subsequently improve the gel strength.

Agarose is typically a high molecular weight polymer (>100kDa) and is low in sulphate whereas agaropectin is typically low molecular weight (<20kDa), high in sulphate (ca. 5-8%) and is non-gelling.



Structure of agarose showing repeating units of agarobiose

A note on Danish agar – Danish agar is the traditional name for a gelling polysaccharide that is extracted from *Furcellaria* seaweeds known as furcellaran. Furcellaran is not an agar, it is a kappa-beta type carrageenan that has had historical use in the Baltic regions of Europe. These days there is a small extraction industry in Estonia.

Production

Most of the world's agar is sourced from cultivated species of *Gracilaria.* Over 95% is grown in China and small amounts are cultivated or harvested elsewhere *e.g.* Chile.

Agar is also extracted from other species including *Gelidium, Pterocladia, Gelidiella & Ahnfeltia.* These seaweeds are typically wild harvested in Chile, Morocco, South Africa, France, Spain & Portugal.

🡐 Dried *Gracilaria* seaweed – used for agar extraction

Agar can be extracted in a variety of ways, but the basic methodology revolves around dissolving the agar from the seaweed with hot water, separating the agar from the cell wall residues by filtration and then isolating the agar from the dilute solution. Various methods have been developed to isolate the agar from solution, the traditional method relies on cutting the gel into strips and allowing it to freeze overnight and thaw out the next day in the sun. Due to the high level of syneresis produced in an agar gel the strips loose water on each freezing and cooling cycle until a dry strip is formed. this strip is known in Japanese as *Kanten* which literally translates as "Frozen sky". Traditional agar is sold in strip or block form.

Agar can be made in several ways at industrial scale. One method involves freezing agar

solutions in ice tanks in a simply scaled up version of the traditional method. A newer method, which only works for agar types that have significant syneresis such as *Gracilaria,* involves forming blocks of gel that are wrapped in cloth and pressed to remove the water. The pressing is usually done with large static concrete weights. The pressed agar is usually pressed again in hydraulic presses to reduce the water content even further prior to drying. The dried agar is then milled into a coarse powder. The gel press method is the also basis for gel press methods used in carrageenan processing.

A variation of the gel pressing method involves pumping broken agar gel into large filter presses and using the pressure from the feed pumps to force water out of the matrix. This technology was pioneered by Hispanagar in the 1960's and is now the dominant method of pressing agar. Another methodology involves roller drying the extracted agar. This method has the advantage in that it can utilise a variety of agar species including *Gelidium* which cannot be pressed easily.

Agars derived from *Gelidium* seaweeds are naturally more functional than those from *Gracilaria* and other seaweeds, thus additional processing steps are typically required to improve the gelling potential.

Gel strength can be improved by removing some of the ester sulphates from the agar chain by alkali treatment. Alkali treatment also increases syneresis and makes pressing the agar easier.

🡐 Dried *Gelidium* seaweed – used for agar extraction

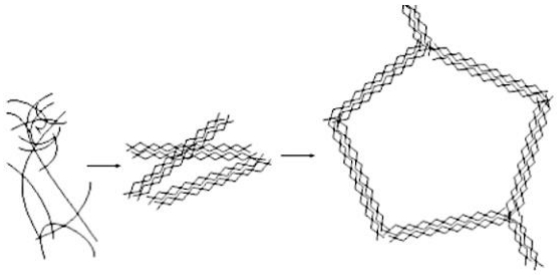
Properties

Agar gels due to the presence of the agarose fraction in the crude agar, at typical concentrations between 0.5% and 2.0%. Unlike carrageenan, agar does not require the presence of any particular ions to gel. One of the classic uses of agar is for the preparation of microbial plates where the combined properties of low syneresis, no dependence on ions and low set temperature make agar ideal.

Agar has a uniquely high hysteresis between its melting and setting temperature. Typically, agar needs to be heated above 90^0C to form a good solution and depending on the seaweed source the setting temperate can be as low as 30^0C but is typically between 30-45^0C for a 1.5% solution. To overcome the very high dissolution temperature of agar, several companies manufacture a form of agar that has been specially dried to allow the agar to dissolve at lower temperatures.

🡐 Classical use of agar - microbial grade

According to Rees, agar forms antisymmetric double helices on cooling that hydrogen bond to form aggregations. These aggregations can then form larger groupings to give a large reticulate, porous gel structure. This porous gel structure has the unusual property of behaving like a sponge. An agar gel of a particular shape can be dried and upon rehydration it will swell to its original size and shape.



Aggregation of agar helices to form a reticulate structure

Unlike some other hydrocolloids, agar does not show many commercially significant synergistic properties. It does show synergy with sucrose and this is exploited in some confectionery products. *Gelidium* agar is known to form a small synergistic interaction with locust bean gum that is not seen in products based on *Gracilaria*. Synergy has been reported between low gel strength agar and guar gum in a patent by Rachid Lebbar of Setexam.

Agar is reasonably acid stable compared to other polysaccharides and does not show any protein reactivity. It can be used in acidic dairy products such as yoghurts where carrageenan would cause excessive flocculation due to the protein reactivity of the carrageenan.

References

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