Acidified Milk Products and Protein Stabilisation
Pectin is a natural fruit ingredient and is therefore a perfect fit with the positive image of acidified yoghurt fruit drinks. Stabilisation with pectin is both efficient and economical.

Pectins for acidified milk products

As a stabilising agent requiring minimum dosage, pectin allows for an economical and efficient stabilisation of products over a duration of several weeks - products which, if not stabilised, would not look appealing.

Pectin in milk products

- Pectin prevents the agglomeration of proteins and thus the phase separation and whey separation at low pH-values (e.g. in yoghurts and milk fruit drinks).
- On account of its thickening effect pectin is used to create a specific mouthfeel (e.g. smoothies)
- Pectin provides texture and prevents syneresis (e.g. in set and stirred yoghurt)

Milk products: healthy and convenient

Nowadays, less and less time is spent on preparing food and consuming it. The reasons for this and consequences thereof are widely discussed. One thing, however, is certain: foods that can be consumed immediately, especially away from home, are spot-on in the trend of "convenience". A good example is the mobile breakfast in the form of yoghurt drinks that can be consumed in the underground, in your car or even on your bike.

Despite of, or maybe just because of its dwindling importance, breakfast is expected to provide people with a healthy start into the new day, equipping them with everything they need for their daily routine. Is there any family of products with a better image in this respect than milk-based products, especially when they also contain fruit? Closely related in taste to a home-made breakfast of fruit and yoghurt, these drinkable or spoonable snacks give you the feeling that, despite today’s hectic pace and pressure to save time, you have done something good for your health.

The countless possibilities for innovation provide this food sector with additional momentum. The range of potential ingredients is enormous: not only fruit components but also many functional ingredients can be added too. In their selection of protein components, manufacturers have almost unlimited freedom in controlling the flavour, texture and sensory perception of the product.

The consequence of these consumer and market trends is that yoghurt, milk, whey and also other protein sources such as soy, are increasingly being combined with fruit. Pectin has long been established as a stabilising agent in this combination, and for good reason. As a natural fruit ingredient with a generally positive reputation, pectin is a perfect fit for the product image.
Pectin structure

Pectin is found in the cell walls of most higher land plants, contributing to many cell wall functions. It provides both structure and texture, it controls the plants’ water balance on account of its swellability and colloid nature and it protects plants from microbiological infections and injuries.

The pectin used in foods is a high-molecular heteropolysaccharide with galacturonic acids as its main component (at least 65%). The acid groups can be free (i.e. in the form of sodium, potassium, calcium or ammonium salt) or can be naturally esterified with methanol. Pectin is obtained from the cell wall by acid extraction and contains a variety of neutral sugars, mostly rhamnose (in the main chain), galactose, arabinose as well as small amounts of other sugars (as side chains). The neutral sugars are fragments of the original plant cell wall structure and are distributed over the polygalacturonic acid molecule as side chains of different branching points and lengths. Regions rich in neutral sugars (so-called “hairy regions”) alternate with homogenous polygalacturonic acid regions (so-called “smooth regions”).

The proportion of neutral sugar side chains in the total pectin molecule, i.e. the ratio of hairy regions and smooth regions, is dependent on the raw material used and on the manufacturing conditions, such as under hot, acid conditions - the standard extraction conditions for commercial pectins - many side chains of neutral sugars are cut off, and the more acid-resistant polygalacturonic acid chains are extracted as soluble pectin.

High-quality pectins have a high content of galacturonic acid, i.e. pronounced smooth regions and as little neutral sugar as possible.

The galacturonic acid groups in the pectin chain are partially esterified with methanol. The degree of esterification determines the functional properties. Pectins with a degree of esterification exceeding 50% are classified as high methylester pectins, pectins with a degree of esterification of less than 50% are classified as low methylester pectins.

In the case of high methylester pectins the distribution of the free acid groups over the polygalacturonic acid chain - which may be random or block-wise - has a significant effect on the functional properties, especially on the stabilising properties of acidified, protein-rich products. A block by block distribution of the free carboxyl (or acid) groups generates regions with a higher electric charge density at the pectin molecule, i.e. regions with a stronger affinity to the protein molecule, which, under acid conditions, is positively charged. Pectins are synthesised completely esterified in the cell wall. In high methylester pectins, free acid groups and their distribution over the molecule are caused by the effect of cell wall enzymes (such as pectin methyltransferases) and/or the extraction conditions during the pectin production.

High methylester citrus pectins are particularly suitable for stabilisation of acidified milk products.

A block by block distribution of carboxyl groups in high methylester pectins can be recognised by an increased reactivity with calcium ions, demonstrated by an increase in viscosity in a pectin solution when calcium ions are added. Especially high methylester citrus pectins display calcium reactivity, which is attributable to the activity of the citrus-specific methylesterase.
Pectin production

Industrially manufactured pectins are mainly obtained from apple pomace and citrus peel. The protopectin present in the raw material in water-insoluble form is heated up and extracted as soluble pectin by way of acid hydrolysis. The pectin-rich extract is mechanically cleaned and carefully concentrated. The extraction parameters are optimally balanced to prevent molecular degradation by hydrolysis, for the pectins' gelling strength and stabilisation properties are substantially affected by their molecular weight.

Pectin is insoluble in alcohol. When the aqueous extract is mixed with alcohol, pectin is obtained as a thread-like precipitation, which is subsequently pressed and dried. The dried pectin is ground into a powder, sieved, blended homogeneously and standardised according to the intended application.

Low methylester pectins are obtained by specific acid hydrolysis of the pectin's methylester groups.

Amidated pectins (mostly low methylester pectins) are created by the reaction of suitable high methylester pectins with ammonia. During amidation, part of the methylester groups is converted into amid groups. This changes the gelling properties (in particular reactivity with calcium ions) compared to pectins de-esterified by acid.

Pectin functions

Pectins are used as gelling, thickening and stabilising agents in food. Pectins gel by forming a three-dimensional network by way of reactive zones between pectin chains (bonding zones).

Pectins as gelling agents are used in jams and jelly products, confectionery, in the field of baked products and in household gelling agents. Pectins are also used as thickening agents, e.g. to enhance the mouthfeel in juice drinks. The coagulating effect stems from the high water-binding ability of the large pectin molecule.

In acidified milk products, pectins are used as stabilising agents, where with the low pH-value in yoghurt drinks they protect the casein against flocculation and sedimentation, and, in set yoghurts aid setting and prevent syneresis. Drinks containing flavour oils are also stabilised with pectins. Here, the pectin acts as an emulsifying agent.

High methylester pectins only gel when there is a high content of soluble solids (at least 55%, e.g. sugar) and the pH-value is sufficiently low. A high sugar content dehydrates the pectin molecules, which therefore, can approach each other more easily. The pectin chains are networked together by hydrogen bridges and the interaction between the methylester groups. Acid inhibits the dissociation of the free carboxyl groups whereby the electrostatic repulsion of the otherwise negatively charged pectin chains is mostly avoided, which also favours the convergence of the pectin chains and the formation of bonding zones.

Low methylester pectins also gel according to the aforesaid mechanism. They are, furthermore, able to form bonding zones with polyvalent cations (e.g. calcium ions), i.e. they also gel relatively independently of soluble solids and the pH-value. The reactivity with calcium ions increases as the degree of esterification declines. The optimum amount of calcium ions or the amount of calcium ions required for gelling for a pectin with a specific degree of esterification is dependent on the pH-value of the product, the soluble solids content and on existing buffer elements (e.g. complexants). Amido groups also have an effect on calcium reactivity. Low methylester, amidated pectins form a sufficiently solid jelly even with small amounts of calcium ions, permitting a wider range of calcium concentration, i.e. they are more tolerant towards calcium fluctuations.
Pectins are very stable within a pH-range of 2.5 - 4.5. At pH-values above 5, and accelerated by high temperatures, the esterified galacturonic acid chain can depolymerise due to β-elimination, i.e. the pectin disintegrates. As a result, the pectins lose their gelling strength and stabilising properties. Therefore, in the milk industry pectins are mainly used in acidified products, which as a general rule have a pH-value of approx. 4.

Brief information on acidified milk products and related products
Acidified milk products in which pectins are used can be divided up into fermented acidified milk drinks, directly acidified milk fruit drinks and stirred or set yoghurts.

The classic yoghurt drink but also more exotic products, such as kefir, koumiss or ayran, belong to the fermented acidified milk drinks. These products usually contain a high milk content. In many cases, fruit concentrate or fruit aroma and sugar or sweeteners, but also salt (e.g. ayran) are added.

Directly acidified milk fruit drinks usually have less of a milk character, as a rule the protein content is lower, and the notion of a “refreshing” drink is uppermost. These drinks are often also classified as smoothies, a group which lacks precise definition.

Whey and whey fruit drinks are getting more and more popular. The raw material whey, a by-product of the cheese-making industry, is reasonably priced and, on account of its content of high-grade proteins, is extremely valuable from a nutritional point of view.

For a long time, soy products were almost only of interest to vegetarians or people suffering from allergies or lactose intolerance. New manufacturing technologies to improve the taste of soy products and increasing consumer awareness of the health benefits of soy products are making soy drinks and fruit drinks with soy, in the form of protein-enriched milk drinks, more and more popular.

Yoghurt drinks and milk fruit drinks
The interaction between pectin and casein causes the stabilisation of milk proteins and can be explained as follows:

In milk (pH-value 6.5 - 6.7) the milk proteins, the so-called caseins, are negatively charged. They are mutually repellent, which prevents precipitation. During acidification, the casein micelles lose their negative charge. At the isoelectric point (pH-value 4.6), they have the lowest charge and weakest hydration.
Pectins are used to regulate the viscosity in drinks. Citrus pectins are generally used for low-viscosity drinks, and apple pectins for high-viscosity drinks.

Below the isoelectric point the casein is positively charged.

This leads to a change in the structure, the casein is converted into the flocculating acid casein, calcium is released and a gel is formed. If the gel is mechanically destroyed, a suspension is obtained, which, after a longer resting period, agglomerates anew. When acidified milk products are heated, the proteins will contract due to water loss (dehydration). The proteins take on a sandy structure and are subject to sedimentation.

The use of high methylester pectins in yoghurt drinks, yoghurt fruit drinks and milk fruit drinks prevents the agglomeration of the proteins; in thermised products the proteins are protected against dehydration and sedimentation.

Casein is stabilised as a result of a protective-colloid effect. The negatively charged pectins accumulate around the casein particles, which are positively charged on account of the pH-value of yoghurt drinks. Due to the specific distribution of ester groups in the molecule, pectins have regions of different affinity as regards the protein binding. Regions of high affinity cover the protein surface (electrostatic stabilisation), regions of lower affinity extend out from the surface into the liquid and contribute to a so-called steric stabilisation. The protein contraction caused by water loss during thermisation and the resultant sandy structure of the proteins as well as the agglomeration of the proteins can be prevented by adding high methylester pectins. A specific mouthfeel can also be obtained by adding pectin.

An increase in viscosity also enhances the protein stabilisation in acidified milk drinks. Increased viscosity achieved by adding pectin counteracts the sedimentation of protein agglomerates. High methylester apple pectins are especially suited for this stabilisation mechanism.

If a low-viscosity end product is required, high methylester citrus pectins are mainly used.

**Pectins bond to the positively charged protein surface with the bridges of free carboxyl groups**

**Pectins change the charge distribution on the surface of the casein molecule.**
Only high methylester pectins within a very specific range of esterification (approx. 68 - 72 %) are suited for the stabilisation of acidified milk products. For optimum stabilisation, pectins require a high molecular weight and a defined calcium reactivity. High methylester citrus pectins fulfil these requirements. A low calcium content in pectin (use of deionised pectin) has a positive effect on stabilisation and results in an acidified milk drink of low viscosity.

**Influential parameters in the production of acidified milk drinks**

The pectin dosage required for optimum acidified milk stabilisation depends on the formulation and production technology of the products to be stabilised. Important parameters are:

- pH-value of the drinks
- Protein content
- Fermentation conditions
- Conditions during direct acidification using juice or acid
- Homogenisation
- Thermoisation during the production process
- Thermoisation of the finished products
- Addition of calcium

Protein concentration and protein particle size: the higher the protein content, the higher the pectin dosage required for stabilisation. The protein particle size is influenced by the conditions present during yoghurt fermentation (temperature, time, bacteria cultures used). Fast fermentation (addition of acid for direct acidification) results in large protein particles which are difficult to retain in suspension and which require higher pectin dosages for stabilisation.

**Formulation and technology determine the required pectin dosage.**

Very small protein particles have a relatively large surface and also therefore require more pectin to compensate for the charge of the proteins on the surface. The production of the yoghurt as the basis for creating acidified milk drinks is therefore very important for achieving optimum, uniform-sized protein particles.

Homogenisation: pectins are uniformly distributed on the surface of the protein particles using high pressure. Homogenisation should be performed at a pressure of 150 - 250 bar and at relatively high temperatures (at least 30 - 40°C). When pectin is added in dry form, it must be heated up and dissolved before homogenisation. During this process, the conditions must be such that no changes occur at the protein, such as the formation of larger agglomerates, which can only be stabilised by a higher pectin dosage.

Heat treatment: depending on the desired storage life, different heat treatment methods are applied (pasteurisation, ultra-high temperature processing). The more intense the heat treatment, the greater the risk of thermal agglomeration of the protein particles. Thus, the pectin dosage also depends on the type of heat treatment used.

Yoghurt, whey, soy and other protein-rich milk products combined with fruit ingredients offer a wide variety of possibilities for healthy and innovative products.
Calcium content: an increased calcium content in the drink also requires a higher pectin dosage. In this case, apple pectins can be of advantage as they react less with calcium than citrus pectins. The addition of pectin and calcium must be performed separately during the manufacturing of calcium-enriched drinks, in order to prevent reactions between pectin and calcium.

Assessing the stability of acidified milk drinks
The stability of acidified milk drinks is evaluated on the basis of the viscosity, the amount of sediment after defined centrifugation and by microscopic examination of the protein particles. The chart shows the viscosity of a acidified milk drink in dependence of the pectin dosage.

If the pectin dosage is too low, the protein particles stick to each other due to insufficient stabilisation, resulting in high viscosity. Increasing the pectin concentration enhances stabilisation, as the protein particles are less able to agglomerate. The optimum pectin dosage required for standardisation (OSD) is achieved when viscosity is at its minimum. At this point, on account of the effects described above, the protein particles can repel each other and are thus able to move freely, which lowers the viscosity.

This dosage depends on the type of pectin used, the formulation and the manufacturing parameters. If the pectin dosage is further increased, the pectin’s stabilising properties but also its thickening properties come into effect, increasing the viscosity of the drink. This may be desired or undesired, depending on consumer preference.

The viscosity and sediment of a acidified milk drink as a function of the pectin dosage are used as criteria in assessing the suitability of a pectin and for standardisation. During this process, the so-called “optimum stabilisation dosage” (OSD) is determined, the most important standardisation criterion for pectin for the stabilisation of acidified milk.

Whey drinks
The variety of whey drinks available has increased sharply over the past few years. Whey products have a healthy image, are low in calories and are refreshing. The raw materials for these drinks stem from the cheese-making industry. A distinction is made between sweet whey (with a pH-value above 5.8 - from rennet production) and sour whey (with a pH-value below 4.5 - from sour milk cheese production). Sweet whey powder but also whey concentrates are frequently used in whey fruit drinks.

Whey drinks have a healthy image and, when stabilised with pectin, have a long shelf life.
The heat denaturation of the whey proteins can be prevented or reduced by adding pectin. A partial denaturation during the manufacturing process can lead to the sedimentation of the whey protein. This raw material-dependent sedimentation can be prevented by adding pectin to increase the viscosity.

**Soy products**

As an alternative to milk protein, soy protein can be used in the production of acidified protein-enriched drinks - in the form of soy milk, soy protein isolate and soy protein concentrate. Soy protein isolates and concentrates often do not dissolve easily or completely. Therefore, optimum hydration of the soy proteins is required when creating soy products.

Soy protein can be stabilised under acid conditions, similar to the stabilisation mechanism of milk proteins (its isoelectric point is similar). The insoluble part of soy protein (dependent on the soy product and manufacturing conditions used) can be stabilised by increasing the viscosity.

**Set and stirred yoghurt**

In set yoghurts, low methylester or low methylester amidated pectins are used to increase the firmness and to reduce the tendency to syneresis. The effect of the stabilising agent pectin: a partial coating of the protein surface by the pectin results in protein flocculation, which strengthens the casein network, giving a firm yoghurt. As pectins are hydrocolloids that are soluble in water, they form strong hydrated zones. On the one hand, this results in a creamy mouthfeel, on the other hand, it prevents whey separation. The addition of pectin after fermentation would result in the destruction of the already formed casein gel due to the mechanical stress involved.

The effect of pectins in yoghurts can be determined by ascertaining the firmness, i.e. penetration, in set yoghurts, and the viscosity in stirred yoghurts, and by determining the syneresis. The charts above show the effect of pectin on the firmness and syneresis in yoghurts.

**Pectins stabilise whey and soy proteins in long-life products**

To obtain a stable product, not only the appropriate stabilising agent is an important parameter in the production of whey and whey fruit drinks, but also the selection of the raw materials and the manufacturing technology.
OVERVIEW

Pectins for Milk Products

With its CM/AM product range, H&F offers a variety of pectins to meet the various pectin requirements of acidified milk products, yoghurt, whey, soy products, etc. In addition to this, H&F develops customised pectins for specific customer requirements.

<table>
<thead>
<tr>
<th>Product</th>
<th>Pectins</th>
<th>Properties</th>
<th>Pectin type</th>
<th>Recommended dosage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidified milk drinks, whey drinks, Soy drinks</td>
<td>high methylester pectins</td>
<td>stabilises protein increases viscosity</td>
<td>Classic CM 201 Classic CM 202 Classic CM 203 Instant CM 203 Classic AM 201</td>
<td>0.2-0.5% each, depending on product and process</td>
</tr>
<tr>
<td>Set yoghurt stirred yoghurt</td>
<td>low methylester pectins, low methylester, amidated pectins</td>
<td>increases firmness prevents syneresis</td>
<td>Classic AM 901 Amid CM 020</td>
<td>0.1-0.2%</td>
</tr>
</tbody>
</table>
**Recipe**

**Product**  High-Protein Yoghurt Fruit Drink

- 3g Pectin (0.3%)
- Pectin Classic CM 203
- 800g skimmed milk yoghurt
- 12g fruit juice concentrate, approx. 65% soluble solids
- 80g sucrose
- 105g water
- citric acid solution 50% / tri sodium citrate 10%
- to adjust the pH-value

net weight: approx. 1000g  
pH-value: approx. 3.8 - 4.0

**Manufacturing:**

- Mix dry pectin and sugar
- Stir pectin-sugar mix into yoghurt with a high-speed blender and let the mixture swell for about 30 minutes for better solubility
- Add fruit juice concentrate and water
- Check pH-value, if necessary adjust by adding citric acid solution / tri sodium citrate
- Heat the batch to 70°C while stirring
- Homogenise at 150 bar
- Pasteurise, fill into containers and leave to cool to 20°C

Depending on the type of heat treatment used (pasteurisation, UHT, etc.), the resultant products can be kept between several weeks in cold storage and up to six months and more at room temperature. In the case of products enriched with calcium it is recommended to add the calcium via the milk or the yoghurt. A higher pectin dosage may be required, depending on the amount of calcium added.

---

**Recipe**

**Product**  Milk Fruit Drink, Directly Acidified

- 120g pectin solution 3% (0.4%)
- Pectin Classic CM 201
- 50g skimmed milk powder
- 300g fruit juice, approx. 12% soluble solids
- 40g sucrose
- 450g water
- citric acid solution 50%
- to adjust the pH-value

net weight: approx. 1000g  
pH-value: approx. 4.0

**Manufacturing:**

- Make pectin solution 3% (see Technical Application Information)
- Dissolve skimmed milk powder in water
- Add pectin solution to skimmed milk
- Mix fruit juice and sucrose and stir slowly into above mixture
- Slowly add citric acid solution to adjust the pH-value
- Homogenise at 150 - 200 bar
- Pasteurise
- Fill into containers
- Leave to cool

During the production of directly acidified milk fruit drinks, pectin may also be added with the fruit juice or dispersed as syrup in the fruit juice concentrate.
### Recipe: Whey Fruit Drink

- **Product**: Whey Fruit Drink

  - 120g pectin solution 2.5% (0.3%)
    - Pectin Classic CM 203
  - 30g sweet-whey powder
  - 70g orange juice concentrate
  - 50g sucrose
  - 1.25g citric acid
  - 730g water

  - citric acid solution 50%
  - to adjust the pH-value

  - net weight: approx. 1000g
  - pH-value: approx. 3.8 - 4.0

**Manufacturing:**
- Dissolve whey powder in 470g water and leave to swell for 30 minutes
- Dissolve orange juice concentrate, sugar and citric acid in the remaining water
- Make pectin solution 2.5% (see Technical Application Information)
- Stir pectin solution into the whey (Ultra Turrax®)
- Slowly add orange juice solution, stirring all the time (Ultra Turrax®)
- If necessary, adjust pH-value to 3.8 - 4.0
- Homogenise at 150 bar
- Pasteurise at 70°C for 10 minutes

Whey protein concentrate or sour whey is often used instead of sweet-whey powder. Quite frequently, mixed-whey products are used which in addition to whey also contain milk and/or yoghurt as recipe ingredients.

### Recipe: Soy Protein Drink

- **Product**: Soy Protein Drink

  - 120g pectin solution 2.5% (0.3%)
    - Pectin Classic CM 203
  - 37g soy protein isolate (approx. 85% protein content)
  - 175g fruit juice
  - 75g sucrose
  - 600g water

  - citric acid solution 50%
  - to adjust the pH-value
  - net weight: approx. 1000g
  - pH-value: approx. 3.8

**Manufacturing:**
- Make pectin solution (see Technical Application Information)
- Heat water to 60°C
- Dissolve soy protein in water and leave to swell for 20 minutes (60°C)
- Homogenise at 250 bar
- Add sugar
- Add pectin solution to soy protein solution and stir for 10 minutes (Ultra Turrax®)
- Stir in fruit juice and citric acid
- check the pH-value and, if necessary, adjust with citric acid solution
- Homogenise at 150 - 200 bar
- Pasteurise
- Fill into containers
- Leave to cool

Soy proteins are mostly used in the form of soy protein concentrates or soy milk. Soy protein isolates or concentrates often do not dissolve completely, therefore they require optimum hydration.
**Recipe**

<table>
<thead>
<tr>
<th>Product</th>
<th><strong>Set and Stirred Yoghurt</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2g pectin (0.12%)</td>
<td></td>
</tr>
<tr>
<td>Pectin Amid CM 020</td>
<td></td>
</tr>
<tr>
<td>30g skimmed milk powder</td>
<td></td>
</tr>
<tr>
<td>60g sucrose</td>
<td></td>
</tr>
<tr>
<td>909g whole milk</td>
<td></td>
</tr>
<tr>
<td>yoghurt culture</td>
<td></td>
</tr>
</tbody>
</table>

**Manufacturing:**

- Mix dry ingredients (pectin, skimmed milk powder and sugar)
- Stir mixture into cold milk (Ultra Turrax®)
- Leave to swell for 1 hour
- Heat solution to 85°C, 20 minutes
- Homogenise at 100 bar
- Leave to cool to 43 - 45°C
- Add yoghurt culture, fill into containers
- Allow to ferment to a pH-value of 4.5 - 4.6
- Leave yoghurt to cool to 7°C

During production of stirred yoghurt, the mixture is stirred to a smooth substance after fermentation, left to cool to 20°C, after which the fruit preparation (20%) is added and the yoghurt filled into containers.

In set and stirred yoghurts, pectins are used to provide texture and prevent syneresis.

Apart from offering a wide variety of applications and technological potential, pectins, as natural food additives, provide the great benefit of consumer-friendly labelling.