Walnut Sap and the Pectin Problem

By:

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What we know about pectin as it pertains to sap:

What we know generically as pectin is a term for a family of molecules that all have commonalities and differences. All pectins are long chain polysaccharides that have a high but variable molecular weight, ranging from 50,000 to 180,000 grams/mole. Water by contrast, (which is 98% of sap) has a molecular weight of 18, and sucrose, (the other 2% of sap), has a molecular weight of 342 grams/mole. So, pectin is very heavy. All pectins are built around a common base of galacturonic acid.

Pectins are naturally found in plant cell walls, where the long chain molecule serves as a glue to bind adjacent cell walls. Although pectin is used in cosmetics and has medicinal properties, its most common use is in making jelly. Fruits that are naturally low in pectin, such as cherries and blackberries, need a commercial pectin additive to gel, whereas high pectin fruits, citrus and apples, gel naturally. Commercial pectin is often made from grapefruit rinds and the inner white of a lemon peel can contain as much as 30% pectin.

Pectin gels when heated in a low pH environment with a high concentration of sugars. That is exactly the environment we have as we heat sap in an evaporator. Given those conditions the pectin molecules form a 3-dimensional matrix capturing sugar molecules, and in jams pieces of fruit, and holding them in suspension.

Pectin in sap:

Sap has a low sugar content (2% approximately) and is slightly acidic. Walnut and beech sap are known to contain appreciable amounts of pectin. That is at least enough to cause problems when trying to concentrate the sugars with an RO. Maple and birch do not. That's not to say maple and birch sap does not have any pectin, just that it's not a problem. The RO problem specifically is that the large pectin molecules plug the pores on the semi-permeable RO membranes. Sucrose, a much smaller molecule, also plugs the pores, but it takes a lot longer. It has been reported that rinsing and washing an RO membrane cleans off the pectin just as it does the sugar buildup. That cleaning process is known a desugaring the membrane.

That process is often improperly referred to as backwashing the membrane. It's not. We don't wash backwards through the membrane as you would a pool filter but use water to scour the sugars off the surface of the membrane. One question we need to answer is how effectively desugaring removes pectin from the membrane.

Pectin in sap could be related to the injury caused by tapping and the tree's response to injury. Another interesting question is: "is there pectin in walnut sap of an uninjured (untapped) walnut tree." Our dissection studies show that walnut, with its high pectin sap, is much better in responding to injury than the low sap pectin maple. It has been reported that the amount of pectin, as measured by how long it takes an RO membrane to plug, varies tree to tree and by time in the sap flow season. These are informal observations and need to be substantiated with a rigorous study.

Last summer Hyden Odell at Marshall University conducted a centrifuge study on clear walnut sap. Spinning a 2ml sample at 14,500xg forces he was able to separate out a pellet that is presumed to be pectin. When dried and weighed the sample had a pectin concentration of 0.2mg/ml or 200ppm. Hayden found no difference between early season and late season sap. Spinning at 8,000xg he spun out a 0.1 mg/ml pellet.

Pectin in syrup:
If plugging the RO was not bad enough, pectin will also plug your filter press. In an evaporator the slightly acidic sap goes through a series of chemical reactions first raising its pH and lowering it again to the acidic side. As the sugars concentrate and the pH drops the pectin begins to gel. During the 2021 season Kate Fotos began referring to the gelling pectin as "jelly fish." There were visible semi-transparent globules rising and falling in the concentrating sap. Sarah Collins-Simmons found that when quiescent between boiling a pectin layer rose to the surface. Both the "jelly fish" and the pectin layer could be skimmed off.

The finished walnut syrup needs to be filtered to remove precipitated inorganic solids known as niter or sugar sand. As the sap becoming syrup continues to concentrate with the evaporation of water the "Jelly fish" can congeal and when cooled result in a fine batch of walnut jelly. If the sap happened to be low in pectin it might not congeal but could quickly plug your filters. Then you have syrup, but you also have sediment because it can't easily be filtered. Much of the sediment will, with time, settle out but some will remain suspended resulting in a dark cloudy syrup.

Barbara Leidhl (West Virginia State University) in an earlier study found that she could spin unfiltered walnut syrup in a centrifuge and obtain a distinct grey layer in the plug that was presumed to be pectin.

The pectin measurement problem:
Note that whenever we referred to a pectin plug we modified it with the qualifying statement "presumed to be." That's because to find out how much pectin you have you have to quantify how much galacturonic acid you have, and that is not easy. Short of putting a full-scale organic chemistry lab in your sugarbush, pectin quantification seems impossible. The most technologically advanced instruments most syrup makers have access to is a refractometer. Because polysaccharides are sugars, and so is sucrose, over the summer we asked Hayden to see if light refraction measured with a brix refractometer could be used to quantify pectin. His

study found that it could not, the issue being that although galacturonic acid is a sugar, it is not sucrose. It should be noted that neither can glucose be quantified with a brix refractometer.

However, the centrifuge work Hayden did on walnut sap could lead to an answer. At 8,500g he weighed a pellet and determined a concentration of 0.1mg/l. Spinning at 14,500 he had a plug that weighed 0.2mg/l. The faster spin pulled out more pectin. The efficacy of a centrifuge is a factor of its spin rate and the length of time it is spun, which is related to the feed rate on a flow through system.

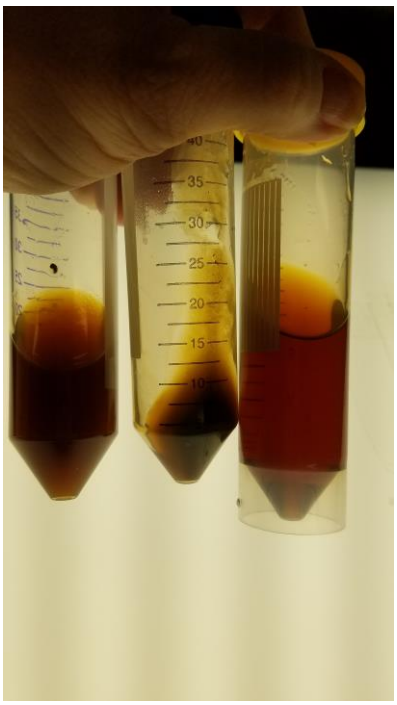
The Extreme Raw Power centrifuge we are working with at Greg Christian's spins at 2,800xg. Larger flow through machines can be purchased that can get up t0 8,000xg. The photo below shows a cream separator that achieved a separation from a high concentration pectin solution. The point is that it looks like we can achieve a separation of pectin from raw walnut sap. And, that we can measure the amount with a high-speed desk centrifuge.

We don't need an absolute number on the amount of pectin in the sap, just a relative number to show if the amount of pectin has been lowered. There are any number of centrifuges for sale online for less than $500 that will spin up to 4,000g holding 15ml samples. The increased sample size with a longer spin time could compensate for the slower spin rate and be an economical way for a syrup maker determine the amount of pectin in his or her sap by simply looking at the size of the pectin plug.

The questions that remain are how much separation, at what speed, and at what flow rate.

Cream separator Centrifuge

Barbara Leidhl's centrifuged walnut syrup



A Breakthrough:
Last week Hayden used a titrimetric technique and was able to positively identify pectin in a solution. His next step is to use that technique to identify pectin in walnut sap. If we can do that, we can eliminate the qualifier "presumed to be" from our description of the centrifuge plug. Once we have done that we should be able to quantify the amount of pectin in a sample by the size of the plug. It's a visual estimate, but it may be good enough for our purposes.

Next Steps:
The next question is, can a continuous flow centrifuge, like an extreme raw power machine, or a supped-up model if it, spin out enough pectin to allow it to be run through an RO?

To answer that we need to:
1. spin some walnut sap in Greg's centrifuge and then spin the "depectinated" sap in a lab centrifuge (14,000xg) and see if it is less than the amount previously measured 0.2mg/l.

2. Measure and photograph the size of the plug (14,000xg) before and after being spun in Greg's centrifuge.

3. Keeping volume and time constant develop a curve that equates g forces to quantity of pectin and size of the plug.

4. At a speed and g forces obtainable with an extreme raw power machine, vary spin time and look at weight and size of the pectin plug.

In the field:
If any of the above looks promising, we need to try it in the field. Spinning the sap to remove pectin, measuring the remaining pectin in the "depectinated" sap with a lab centrifuge, and running it through an RO and measuring the time it takes to clog the membrane by the time it takes to raise the pressure to a determined limit.