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Leaching behavior of water-soluble carbohydrates from almond hulls

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ABSTRACT

Over 58% of the dry matter content of the hulls from the commercial almond (*Prunus dulcis* (Miller) D.A. Webb) is soluble in warm water (50–70 °C) extraction. The water-soluble extractables include useful amounts of fermentable sugars (glucose, fructose, sucrose), sugar alcohols (inositol and sorbitol), polysaccharides, and other components. Extraction rate data were taken over a range of temperatures and particle sizes (including whole hulls). Equilibrium concentrations and liquid retention data were taken over a wide solubles concentration range, enabling use of a standard leaching model for the calculation of stage-to-stage concentrations and flows in an ideal countercurrent extractor. The relations between recovery, product concentration, number of ideal stages, and ratio of solvent-to-feed were determined using the model. The data indicate that a solutes concentration of 18–20% dry matter in the concentrate liquid is attainable. Due to the nature of the native hulls to preferentially absorb water from dilute solutions, initial contact of hulls with the overhead liquid concentrate (if well below ~18% solutes) may result in a significant enhancement of overhead concentration.

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1. Introduction

Almonds are a major crop in the U.S. state of California, which accounts for about 80% of the world's production (Almond Board of California, 2012). Almond hulls and shells are high tonnage byproducts of this production. An estimated 1.4 million tonnes of almond hulls were generated in California in 2013 (Offeman et al., 2014). The almond hulls have been shown to contain high levels of the fermentable sugars glucose, fructose and sucrose, and the sugar alcohols inositol and sorbitol (Sequeira and Lew, 1970; Saura-Calixto and Canellas, 1982; Saura-Calixto et al., 1984). Table 1 lists the average values for these components for each of the predominant varieties in California (Offeman et al., 2014). Values are listed on a "hulls only, dry" basis and on an "as is" basis, which takes into account the moisture in the hulls and the shell, twigs and extraneous matter in the "as is" sample.

Leaching is the removal of a soluble fraction, in the form of a solution, from an insoluble, permeable solid phase with which it is associated (Perry et al., 1997). Leaching is used for recovering, for example, sucrose from sugarcane and sugar beets, gold, uranium and other metals from ores, and vegetable oils from oil seeds. A pretreatment such as milling, cutting or flaking is often used to increase the surface area available for mass transfer. Leaching is known by other names, depending on the industry: extraction, decoction, lixiviation, percolation, infusion, elutriation, decantation and settling (Prabhudesai, 1979). The nomenclature for leaching equipment also varies between industries. For example, in the sugar industry, the leaching unit is known as a diffuser. Leaching of vegetative matter, such as sugarcane, involves a relatively fast dissolution of solubles from between the cells, and a slower diffusion of solubles through cell walls (Rein and Woodburn, 1974).

Leaching may be carried out in batch, semi-batch, or continuous cross-current or counter-current processes. A series of batch extraction vessels, called a Shanks or Roberts battery, can be set up to mimic a continuous countercurrent process. In the literature on extraction from almond hulls, the method used is almost exclusively a batch process, or a series of batch operations, since in general the intent has been analytical: the characterization of hulls. Due to its efficiency, a continuous countercurrent process is desirable. Additionally, a countercurrent process will generate a much more concentrated extract solution then will a co-current process. Two patents aimed at recovery of sugars and/or inositol from almond hulls mention countercurrent extraction (Rabinowitz, 1991, 2004), and describe the general method, but do not supply the basic information needed to design a countercurrent leaching unit.

A common practice in modeling a countercurrent leaching unit is to carry out stage-to-stage calculations, either by graphical or algebraic means, in a similar vein to the methods used in liquid–liquid solvent extraction or distillation. The method uses

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Table 1
Fermentable sugars and sugar alcohols, % (wt), in hulls only, dry basis, and in "as is" samples (Offeman et al., 2014).

Variety	No. samples	% hulls in sample	% DM in hulls	% in hulls only, dry basis			% in "as is" sample		
				Fermentable sugars[a]	Inositol	Sorbitol	Fermentable sugars[a]	Inositol	Sorbitol
Nonpareil	36	95.5 ± 3.3	86.7 ± 3.1	32.7 ± 7.0	2.6	6.1	27.1 ± 6.0	2.1	5.1
Butte	17	85.3 ± 7.9	87.9 ± 2.0	30.3 ± 3.3	1.1	4.0	22.7 ± 3.3	0.8	3.0
Padre	16	87.0 ± 7.9	85.9 ± 3.2	26.6 ± 9.8	0.9	5.2	19.9 ± 7.6	0.7	3.9
Carmel	25	94.1 ± 4.3	88.2 ± 3.0	25.4 ± 4.7	2.1	3.0	21.1 ± 4.1	1.8	2.5
Monterey	21	92.6 ± 5.2	87.3 ± 3.2	25.3 ± 3.7	1.5	3.8	20.5 ± 3.3	1.2	3.1
Fritz	11	96.6 ± 1.6	87.0 ± 2.3	26.5 ± 3.9	0.8	2.5	22.3 ± 3.4	0.7	2.1

[a] Fermentable sugars: sucrose, glucose, fructose.

mass balances (the operating line) and equilibrium relationships to determine concentrations and flows for one stage based on the concentrations and flows in the previous stage and the external material balance. In leaching, an additional relationship is required, which is the amount of liquid retained by the solid phase as it progresses from stage to stage. Leaching, then, combines solution and diffusion of solute from the solid phase, and washing of the liquid retained by the solid phase (Rein and Woodburn, 1974).

The objectives of this study are to (1) develop information on extraction rate behavior of water-soluble material for a range of temperatures and particle sizes, including whole hulls, (2) determine the "equilibrium" and liquid retention on the solid phase for a range of solute concentrations, and (3) use these data in a countercurrent leaching model to calculate flows, compositions, and the number of ideal stages for a range of operating parameters to aid in determining the practicality of recovering the soluble material.

2. Theory

Three components are considered: W, the solvent (water); *S*, the solutes (polysaccharides, mono- and disaccharides, sugar alcohols, a portion of the ash, and other water-soluble materials); and *I*, the inerts (the portion of the hulls that does not dissolve). In the equations below, all flows and concentrations are on an inerts-free basis. The overflow *V* is the liquid solution composed of solute and water. Flowing in the opposite direction is the solid phase entraining some solution, the underflow. This phase, *L*, being on an inerts-free basis, is composed of solute and water. The underflow *L* comprises both the undissolved solute and absorbed water, and the liquid retained by the solid, in its pores and clinging as a film to its surface, and in the interstices between particles. In the standard leaching treatment, it is assumed that the inerts are not soluble or entrained by the overflow *V*, and that the flow of inerts from stage-to-stage is constant. Fig. 1 displays a classic countercurrent leaching cascade of *N* stages (McCabe and Smith, 1967; Prabhudesai, 1979). Referring to this figure, The external total mass balance is

$$L_0 + V_{N+1} = L_N + V_1 \qquad (1)$$

For stages 1 through the intermediate stage *n*, the total mass balance is

$$L_0 + V_{n+1} = L_n + V_1 \qquad (2)$$

And the solute mass balance is

$$x_0 L_0 + y_{n+1} V_{n+1} = x_n L_n + y_1 V_1 \qquad (3)$$

After McCabe and Smith (1967), the equation for the operating line is generated from the total and solute material balances around stages 1 through *n*

$$y_{n+1} = \frac{L_n}{L_n + V_1 - L_0} x_n + \frac{y_1 V_1 - x_0 L_0}{L_n + V_1 - L_0} \qquad (4)$$

From Eq. (4), the composition of the overflow stream from stage $n+1$ can be calculated from the composition of the underflow stream from stage *n*, plus knowledge of the external flows and compositions, and the total underflow from stage *n*. Equilibrium data are collected and relate x_n to y_n in each stage. Liquid retention data are collected and relate L_n to y_n and the inerts present in the stage.

In ideal leaching, $x_n = y_n$. In other words, all solute is dissolved, and the solute concentration in the overflow equals that of the underflow in each stage, on an inerts-free basis. Subsequent stages after the first are merely washing steps to reduce the concentration of solute in the solution entrained by the solid phase. However, true equilibrium may not be achieved due to incomplete mixing and insufficient time for complete diffusion of solute and water to take place. The "equilibrium" data described later and used in the model are taken at a point in time for each equilibration that may be less than that needed to achieve true equilibrium.

Constant underflow is not assumed. The density and viscosity of the overflow in each stage varies with the solute concentration, which affects its ability to drain from the solid phase. Also, the ability of the solid phase to retain liquid changes due to swelling of the hulls, changes in porosity, and perhaps other factors as the solids progress from stage to stage. This is particularly true for stage 1, the initial contact of the hulls with liquid, where there may be substantial absorption of liquid by the hulls. The underflow data must be measured, and is usually related to the mass of inerts present in the underflow, and the solute composition of the overflow in equilibrium with it.

3. Materials and methods

3.1. Extraction rate runs

Nonpareil variety ripe almond fruit was harvested in Fall 2011, hulled by Central Valley Almond Association, McFarland, Kern County, California, and the hulls stored in large piles outdoors (standard practice in this dry region) for approximately 3 months. A sample was obtained on 20 December 2011 from the pile. The sample was stored in the lab for 6 months and hand-sorted into fractions: hulls, shells, twigs, and other. A portion of the hull fraction was milled in a Waring blender and screened into the following particle size ranges: −1/4″/+6 mesh (3.35–6.35 mm), −6/+8 mesh (2.36–3.35 mm), −8/+10 mesh (2.00–2.36 mm), and −10/+12 mesh (1.70–2.00 mm).

A 1 liter 3-neck flask was placed in a pre-heated water bath. The flask was equipped with a stirrer and condenser to minimize evaporative losses. Hot water (665 mL) was added and the temperature adjusted to 40, 55, or 70 °C. Whole or milled almond hulls (35 g) were added and stirred at 60 RPM for 6 h. Samples of the liquid phase were drawn periodically through a 0.45 μm syringe filter for Brix and % dry matter (%DM) determination. For a few runs, sugars analyses were also performed.

3.2. Equilibration runs

Nonpareil variety ripe almond fruit was harvested and hulled between 15 August 2013 and 15 September 2013 by Cortina Hulling

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