Industrial Crops and Products 54 (2014) 109–114

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Almond hulls as a biofuels feedstock: Variations in carbohydrates by variety and location in California

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ARTICLE INFO

Article history:
Received 6 August 2013
Received in revised form 7 December 2013
Accepted 3 January 2014
Available online 31 January 2014

Keywords:
Almond hulls
Carbohydrates
Sugars
Sugar alcohols
Survey
Biofuels feedstock

ABSTRACT

Hulls of the almond (*Prunus dulcis* (Miller) D.A. Webb) have a high content of fermentable sugars (glucose, fructose, sucrose), and are a potential feedstock for biofuels and other uses. The state of California in the United States produces the majority of the world's almonds. Six almond varieties across seven counties in California were studied to assess the amount and variability of sugars and sugar alcohols in the hulls. Previous studies were done over 30 years ago, and don't reflect the current range of varieties and locations. Fermentable sugars ranged from 25 to 33% of the dry weight of the hulls portion of the samples. The "as is" samples contain shells, twigs and other materials that can dilute the concentration of sugars; the Butte and Padre varieties have much higher amounts of shell than the other varieties studied. The Nonpareil variety has the highest fermentable sugars content at an average of 271 kg per tonne of "as is" hulls. Average theoretical ethanol yields ranged from 176 to 130 L/tonne, depending on variety. Finding an economic outlet for the wet, spent hulls is a concern.

Published by Elsevier B.V.

1. Introduction

Approximately 80% of the world's supply of almonds is produced in the U.S., in the state of California's San Joaquin Valley and Sacramento Valley regions (Almond Board of California, 2012). California production for the 2013 crop year is forecast to be 1.85 billion lbs (0.84 billion kg) of almond kernels (National Agricultural Statistics Service, 2013), and is a doubling of production since 2004. The estimated volumes of byproducts are 1.4 million tonnes of almond hulls and 0.55 million tonnes of almond shells, based on Kodad et al. (2008), adjusted by relative production volumes of the different varieties.

The most commonly accepted genus and species name for commercially produced almond is *Prunus dulcis* (Miller) D.A. Webb, however synonyms commonly used in central Asia and China include *Prunus amygdalus* Batsch, *Amygdalus communis* L., and *Amygdalus dulcis* Mill.

In California, the primary varieties that are grown are not self-fertile, and cross-pollination by another variety is required for fruit production. Hence two or more almond varieties are grown in each orchard. When the hulls have split open, the grower mechanically shakes the trees to remove the fruit. The fruit is left on the ground from several days to two weeks to dry. The fruit is then collected and transported to a local plant where the hulls are removed. Generally, the plant will also remove the shell, though in-shell nuts are also produced, usually for export. The plant sells the byproduct hulls and shells, which offsets most of the cost of the operation. The hulls contain simple sugars, and are sold as a component of livestock feed, primarily to dairies. The shells are sold to dairies as bedding material, due to their moisture absorptivity, and to power plants as fuel. Some varieties, notably Butte and Padre, have shell or shell portions which adhere to the hulls. Almond hulls are regulated by the California Department of Food and Agriculture, and almond hulls, commonly called "Prime Hulls", have a maximum of 15% fiber. Too much shell will change the designation to "Hulls and Shell", at 15 to 29% fiber, which commands a lower value than prime hulls.

The industry is interested in exploring alternative uses for these byproducts. The high sugars content of the hulls makes them a candidate feedstock for biofuels production and other uses, but how the sugars content varies between almond varieties, growing locations and other conditions is not well known. Cruess et al. (1947) and Cruess (1949) found 18.3 to 30.6% sugar content (native basis, ave. 6.5% moisture) in hulls from several regions in California. About 41–45% of ground native hulls were soluble in cold water, and 50–55% in hot water. A table syrup was made from the hulls by water extraction with an approximate yield of 100 gallons of 70 Brix syrup per tonne of hulls (about 417 L/tonne). Aguilar et al. (1984) report soluble sugars ranging from 24 to 32% (dry basis) for 3 varieties, but note that variability even within varieties was

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0926-6690/$ – see front matter. Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.indcrop.2014.01.010

large. Interestingly, they note that exposure of hulls on wire racks to 7.6 cm of rainfall reduced the nutritive value of hulls by at least 25%. Sequeira and Lew (1970) report the sugars found in two samples of hulls from northern California. They found fructose, glucose, sucrose, inositol and sorbitol to total 31.5% (dry basis), and a value of 52.4% for all water-soluble solids. Saura-Calixto and Canellas (1982) and Saura-Calixto et al. (1984) analyzed the water-soluble carbohydrate composition of almond hulls, shells, integument and kernels of mixtures of varieties grown on the island of Mallorca, Spain. For the hull component, they found that the principle sugars and sugar alcohols were fructose, glucose, sucrose, inositol, and sorbitol, with minor amounts of xylose, arabinose and raffinose. The total of these was 26.5% (dry basis). Kodad et al. (2008) attribute wide variations in hull composition to differences in cultivars studied.

The purpose of this paper is to study the variation in hull sugars and sugar alcohols by almond variety, growing location in California, and other factors. Over 30 varieties are grown in California. The 6 varieties with the highest production volumes were chosen for this study. These 6 varieties account for 84% of total California production (Almond Board of California, 2012).

2. Experimental

2.1. Sampling plan

Samples of hulls were collected in both the 2011 and the 2012 harvest. The 2011 samples were primarily Nonpareil variety, the highest volume variety at about 39% of total production. The 2012 samples were Nonpareil, Monterey, Butte, Padre, Carmel, and Fritz, accounting for about 84% production of all varieties. The selection of the counties for sampling for each variety in the 2012 season depended on which were the predominant production areas for that variety. For direct comparison, Nonpareils were sampled in all 7 counties (Kern, Fresno, Madera, Merced, Stanislaus, Colusa, and Glenn), and all 6 varieties were sampled in Kern county. Typically 1 gallon (3.8 L) samples from 5 different growers were taken for each variety in each county. Each sample was collected by personnel at the local hulling/shelling plants. The approximate location of each plant is shown in Fig. 1 Samples were collected at each plant from the elevator to the auger line that transports hulls to the storage piles. In this way, a sample representative of the actual ratios of hulls, shell, twigs, etc. was acquired. Sampling from the storage piles was avoided due to segregation of the components in the pile and potential mixing of hulls from several growers and varieties. Care was taken to avoid collection of "rain damaged" samples. When rainfall (or another source of water) occurs after the fruit is shaken off the tree and is drying on the ground in the orchard, the hulls can become blackened and sugars are reduced, primarily through the action of microbes.

2.2. Sample processing

As-received samples contained varying amounts of hulls, shell, twigs, kernels, in-shells, whole fruit, and other material. In some varieties, where shell or shell fragments adhere to the hulls, the shell was manually separated from the hull. The samples were sorted, and each fraction weighed. Only the hull portion was further processed. Hull moisture (as % dry matter) was determined by drying in a convection oven at 105 °C overnight. Ash content (% dry basis) of the hulls was determined by ashing at 600 °C overnight in a muffle furnace.

The sugars and sugar alcohols were extracted from the hulls portion of each sample with approximately 50 °C hot water. Four extractions were done, as follows: (1) 25 g of as-received hulls were ground with 475 g of hot water in a blender (Ninja Food Processor

Fig. 1. California counties and locations of almond hulling/shelling plants providing samples. 1 = Kern; 2 = Fresno; 3 = Madera/Merced; 4 = Merced/Stanislaus; 5 = Colusa; 6 = Glenn county.

model QB1000 30) for 1 min, then filtered on Whatman #4 paper in a pressure filter (OFI Testing Equipment, Model 140–31). The filtrate was weighed and a sample collected for sugars analysis. (2–3) The solids were returned to the blender, makeup hot water equal to the filtrate was added and the process repeated twice more. (4) For the fourth extraction, the solids were placed in a 1 L autoclave bottle and hot water was added equal to the preceding filtrate volume. This water was first used to rinse the blender to capture any residual material. The bottle was autoclaved for 30 min, with 15 min for a very gradual exhaust period to avoid boil over (L30 cycle). The contents were filtered as above and the filtrate weighed and sampled for analysis. The filter cake was dried overnight at 105 °C in a convection oven to determine the % of dry matter extracted.

2.3. Analysis of filtrates

The concentrations of sugars in the filtrates were analyzed by high pressure liquid chromatography (HPLC), per a National Renewable Energy Laboratory method (Sluiter et al., 2008). Briefly, the instrument was Agilent Technologies 1260 Infinity series HPLC with a refractive index detector. The column was a Bio-Rad 300 mm × 7.8 mm sugar column (Aminex HPX-87P). The mobile phase was water. Calibration was by the external standards method.

3. Results and discussion

3.1. Sampling data

Table 1 shows the sorting data, moisture level, ash content, and amount of solids extracted for each variety. These results are averages across all counties. The relative amount of shell in the samples varied with variety. Some varieties have a tendency for the shell and hull to adhere together more strongly than others, notably Butte and Padre, as reflected by the high shell content in the hull samples. The amount of dry matter extracted from the hull