

Fuel Value of Grape and Apple Processing Wastes

Dried grape and apple press-cakes were converted to carbon products by low-temperature pyrolysis. The calorific value of these products was determined and compared with that of a commercial barbecue briquet. The gross heat of combustion of grape and apple charcoal briquets was approximately 90% of that for the commercial briquet, while the dried press-cakes contained approximately 65%. The thermolytic reactions generally augmented the fuel value of the dried press-cakes by 37–45%.

The press-cake that remains after juice from crushed grapes and apples has been extracted is presently a wasted agricultural resource. It usually contains more than three times its dry weight in liquid. A very limited amount has value as a source of food and medicinal pectin. The remainder is transported to landfills, but disposal in landfills has become environmentally objectionable. Walter and Sherman (1975) facilitated separation of the solids from the liquid medium by charring the solids in situ with sulfuric acid.

Moisture notwithstanding, Hess and Cole (1972) transformed vegetable matter to coke fuel by decarboxylating and carbonizing it in a liquid medium under pressure. Reznikov and Morozov (1966) dried lignin to 10–15% moisture, pyrolyzed it at 550 °C, and briquetted it while hot without the addition of binders.

Carbonized intermediate substances have long been known to yield a larger fraction of combustible matter per unit volume than the starting material (Poole, 1900). Therefore, low-temperature pyrolysis was studied as a method of recovering the fuel value of grape and apple processing wastes.

A major property of grape and apple press-cakes is their generally high concentration of sugar. Pyrolytic events including the development of acidity (Walter and Fagerson, 1970) will transform this sugar to caramels, a widely used class of food additives with the ability to harden at a low pH (Peck, 1955). Naturally occurring pectin in grape and apple press-cake will also form rigid gels in an acidic medium. In the following experiments, these properties were exploited for the purpose of converting the unused by-product into useful carbon briquets.

EXPERIMENTAL SECTION

Proximate Analysis. Soluble carbohydrates were extracted with 60 °C water from 100-g samples of grape and apple press-cake. These were determined by anthrone and glucose standards. Crude fiber, moisture, and ash were determined by official methods (AOAC, 1970).

Briquets. Moist grape and apple press-cake from pilot plant operations in this department was air-dried in a fume hood, and was then heated at 180 ± 20 °C for 1.5 h. A sample of the resulting pyrolyzate was set aside for calorimetry, and the remainder was further heated for conversion to granulated charcoal (Walter and Sherman, 1975).

The air-dried press-cake and charcoal were mixed separately with 10–15% (w/w) of a carbohydrate binder (43° Baume corn syrup, 10% pectin dispersion, or liquid calcium sulfonate). The heated mixture was placed in a briquet mold under a pressure of 5 lb/in.² (0.35 kg/cm²), and was allowed to cool before releasing the pressure.

Calorimetry. One-gram samples of the dried, unheated press-cakes, pyrolyzates, experimental briquets, and a commercial barbecue briquet were combusted in a Parr series 1200 adiabatic calorimeter (Parr Instrument Co.,

Table I. Proximate Analysis of Grape and Apple Press-Cake

	%	
	Apple	Grape
Moisture ^a (105 °C)	76	69
Soluble carbohydrates ^b	35	29
Crude fiber ^b	26	18
Ash ^b	1	6

^a Wet weight basis. ^b Dry weight basis.

Table II. Gross Heat of Combustion of Fuel Items

Items	Btu/lb
Grape press-cake (dried at 105 °C)	8 367
Apple press-cake (dried at 105 °C)	7 960
Grape pyrolyzate	10 564
Apple pyrolyzate	11 506
Grape charcoal briquet	11 470
Apple charcoal briquet	11 522
Commercial briquet	12 832

Moline, Ill.). The calorimeter was standardized with Parr calorific standard benzoic acid pellets. Reagent grade (99.9+%) benzoic acid crystals were then treated as an unknown sample. The gross heat of combustion was calculated for each sample, including the benzoic acid crystals.

RESULTS AND DISCUSSION

The proximate analysis of grape and apple press-cake is summarized in Table I. Retained juice was responsible for the high moisture content. In this condition, these wastes are unacceptable for most commercial or industrial uses.

The standard benzoic acid pellets contained 6318 cal/g. The benzoic acid crystals yielded 6316 cal/g, indicating a relative uncertainty of no more than 1 Btu in 3000 Btu. The calorific value of the fuel items is listed in Table II. It is seen that the gross heat of combustion of grape and apple charcoal briquets was approximately 90% of that for commercial barbecue briquets. The dried press-cakes contained approximately 65%. The thermolytic reactions which resulted in the evolution of water and gases had the effect of increasing the density of combustible carbon atoms, and, consequently, the calorific value of the press-cakes was augmented by 37–45%.

Upon air-drying the solids from 69–76% to 7% moisture, sugar was concentrated approximately tenfold. At 180 °C, this concentrate was transformed to thermoplastic caramels which had enough adhesive strength, when cold, to bind the secondary reaction products. At low temperatures, the added carbohydrate polymers assisted in binding the ligno-cellulosic fibers that escaped thermolysis.

All briquets were stored in an open container for 1 year without disintegration or appreciable weight alteration.

LITERATURE CITED

- Association of Official Analytical Chemists, "Official Methods of Analysis", 11th ed, Washington, D.C., 1970.
 Hess, H. V., Cole, E. L., U.S. Patent 3642458 (1972); *Chem. Abstr.* **76**, 131244Z (1972).
 Peck, F. W., *Food Eng.* **27**, 94 (1955).
 Poole, H., "The Calorific Power of Fuels", 2nd ed, Wiley, New York, N.Y., 1900, p 83.
 Reznikov, V. M., Morozov, E. F., *Khim. Pererab. Drev., Ref. Inform.* **22**, 10 (1966); *Chem. Abstr.* **66**, 77123n (1967).
 Walter, R. H., Fagerson, I. S., *J. Food Sci.* **35**, 606 (1970).

- Walter, R. H., Sherman, R. M., *J. Agric. Food Chem.* **23**, 1218 (1975).

Reginald H. Walter*
Ruth M. Sherman

Department of Food Science and Technology
 New York State Agricultural Experiment Station
 Cornell University
 Geneva, New York 14456

Received for review February 11, 1976. Accepted July 25, 1976.

Boron Contamination from Borosilicate Glass

Data presented indicate the magnitude of the blank error to be anticipated if borosilicate glass is used to collect or store samples for boron analysis. It is obviously preferable to have no contact with borosilicate glass but occasionally this is not practical. Many solutions will not be contaminated by contact with borosilicate glass for short periods of time, especially if they are not basic.

The release of boron from borosilicate glass has been noted by many authors as a source of contamination of aqueous solutions and as a source of error in boron analysis. This is especially serious in the analysis of low-boron plant and animal samples. Little quantitative information on the magnitude of this error could be found. This study determined the extent of boron release from borosilicate glass into various aqueous solutions. We wished to determine what risks could be tolerated in sample handling prior to boron analysis.

EXPERIMENTAL SECTION

The following solutions were stored in 500-ml, previously unused borosilicate glass reagent bottles with ground-glass stoppers: distilled water, 5 M hydrochloric acid, 0.1 M hydrochloric acid, 1 M sodium hydroxide, and 0.1 M sodium hydroxide. Each bottle and stopper was rinsed twice in distilled water and air-dried at 25 °C prior to use. No lubricant was applied to the ground-glass joints. Approximately 300 ml of the indicated solution was placed in the bottle and samples were withdrawn at times between 5 min and 171 days. For the first week the solutions were agitated continuously and thereafter shelved and agitated by hand twice weekly. The laboratory temperature was 20–25 °C. Except for the controlled exposure to borosilicate glass, all solutions were handled and stored in plastic equipment. Boron was determined by the curcumin-oxalic acid procedure described by Johnson and Ulrich (1959).

Standard statistical procedures were used for data analysis.

RESULTS AND DISCUSSION

The standard deviation between replicate bottles gives an estimate of the minimum detectable boron and of the precision of this study. For concentrations of boron below 0.1 µg/ml this standard deviation was 0.011 µg/ml. We could thus determine 0.02 µg of boron per milliliter at the 95% confidence level, setting a minimum detectable boron concentration for our procedure. In samples containing more than 1.0 µg/ml the standard deviation between replicates was 0.29 µg/ml.

The data are summarized in Table I. At sufficiently long times all solutions dissolved measurable boron from

Table I. Extraction of Boron from Borosilicate Glass Bottles^a

Time	Water	HCl		NaOH	
		0.1 M	5 M	0.1 M	1 M
5 min	0	0	0	0	0.03
1 h	0	0	0	0	0.10
1 day	0	0.03	0	0.08	0.65
14 days	0	0.23	0.14	1.16	4.11
28 days	0	0.16		4.01	9.94
45 days		0.13	0.10	5.50	
73 days	0.056		0.25		
158 days	0.065			20.2	
171 days	0.066				

^a Data in micrograms of boron per milliliter of reagent. Each point is the average of results from three bottles.

the borosilicate glass bottles. Boron appeared relatively slowly in water and in hydrochloric acid. Even after 5.5 months water stored in borosilicate glass bottles contained only 0.07 µg/ml. The water could have been stored over 1 month before the boron content would have exceeded the standard deviation between replicate bottles. Hydrochloric acid extracted boron somewhat more rapidly. After storage times of 3–4 months the boron concentrations were 0.1–0.3 µg/ml. Sodium hydroxide extracted boron from borosilicate glass both rapidly and in relatively large amounts. With only 5 min exposure, molar sodium hydroxide contained 0.03 µg/ml. In 0.1 M sodium hydroxide no boron was detected at 1 h but it was easily measurable after 1 day. The molar sodium hydroxide extracted boron in excess of 1 µg/ml in less than 5 days storage while the 0.1 M solution exceeded this amount in 2 weeks. With longer storage the concentration of boron exceeded 10 µg/ml. In all solutions the increase in boron concentration was less at long times indicating a possible approach to equilibrium. These data are greater than, but consistent with, the 1.5 µg/ml reported in a 0.1 M sodium hydroxide solution stored 16 months in borosilicate glass (Pinta, 1971).

Many analytical reagents and unknown samples may not be contaminated by contact with borosilicate glass for short periods of time, especially if the solutions are not basic. One should have no detectable contamination from mo-