Brewers Condensed Solubles. I. Composition and Physical Properties[1]

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ABSTRACT

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Brewers condensed solubles (BCS) were assayed for protein, fat, ash, solids content, carbohydrate components, amino acids, minerals, heavy metals, and water-soluble vitamins. Freezing point, acidity, density, specific heat, thermal conductivity, and water activity of BCS were also determined. The composition and physical and biological properties of BCS show that it can replace cane molasses in formulated feeds and in fermentation media.

Brewers condensed solubles (BCS) are the concentrated suspended and water-soluble by-products from the manufacture of beer. The by-products are principally carbohydrate and protein in the pressing liquors obtained from the dewatering of spent mash. Waste beer in the brewery is also shunted into BCS.

The objectives of this work were to determine the composition and selected physical properties of BCS. The composition determines the nutrient value of BCS for animals and microorganisms, whereas the physical properties are needed by engineers to design storage and handling systems. The composition of BCS varies among breweries, but information in this article can be used to begin a data base on BCS.

MATERIALS AND METHODS

Sample Preparation

Samples of BCS were collected successively on 12 days at the Anheuser-Busch brewery in Merrimack, MA. For each of the 12 samples, three subsamples were taken at various times during the day and composited into a single sample (3 L). The twelve samples were frozen and sent by airfreight to Kansas State University, Manhattan, where they were thawed, stirred vigorously, and subdivided into 50-ml samples that were refrozen to await analysis.

Total, Suspended, and Soluble Solids

Ten grams of BCS was placed in a 100-ml volumetric flask and diluted to 100 ml with water. Total solids were determined by placing duplicate 5-ml aliquots in tared 100-ml beakers and drying at 100° C for 12 hr. The remaining material (90 ml) was centrifuged at $2{,}750 \times g$ for 30 min. Both precipitate and supernatant (measured volume) were saved. The precipitate was resuspended in distilled water (40 ml) and centrifuged again. The supernatant containing the soluble solids (5.0-ml aliquot) and total centrifugate (suspended solids) were then dried to a constant weight at 100° C for 12 hr.

Protein, Carbohydrate, and Fat

The twelve samples were analyzed for protein according to AOAC standard method 10.034 (1960).

Total carbohydrate was determined as described by Dubois et al (1956); glucose was used as a reference standard.

Fat was determined by a slight modification of the method of Folch et al (1957). A 1.000-g sample was diluted to 10 ml with water, and the mixture combined with 19 ml of chloroform-methanol (2:1, v/v). To the resulting mixture was added, with mixing, 10% by volume of $0.1 M$ aqueous potassium chloride. The mixture was centrifuged to give two phases: the top layer was discarded, and the lower layer was mixed with methanol (6 ml) and water (10 ml) and recentrifuged. Again, the top layer was discarded, and the lower layer placed in a tared beaker and dried over a steam bath. The residue was suspended in water (5 ml), and the entire extraction procedure repeated. After one more repetition of the extraction procedure, the organic phase was dried on a steam bath and the residue oven-dried at 100° C for 12 hr.

Ash

Ten grams of BCS was diluted to 100 ml with water, and duplicate aliquots (5 ml) of the mixture were placed in tared ceramic dishes. The solution was dried for 12 hr at 45° C and ashed by conventional means (AOAC 13.006, 1960).

Crude Fiber

Ten to fifteen grams of a sample was placed in a 50-ml beaker and dried to a solid at 80° C. The resulting solid was ground to a powder and crude fiber run according to AOAC method 22.040.

Gross Energy

Gross energy of the 12 samples was done in accordance with ASTM method D-240-76 (1979). Equipment used was a Parr 1341 oxygen-bomb calorimeter (Parr Inst. Co., Moline, IL).

Carbohydrate Profile

The 12 samples of BCS and a composite of the samples were assayed by high-pressure liquid chromatography for dextrose, maltose, maltotriose, and maltodextrins up to and including maltoheptaose. Degree of polymerization (DP) was 7.

Amino Acid Profile

Amino acids of the 12 BCS samples plus a corn sample were analyzed after acid hydrolysis (Liu and Chang 1971) using a Dionex D-300 kit or Component Analyzer (Dionex Corp., Sunnyvale, CA). Tryptophan was determined after base hydrolysis (Hugli and Moore 1972).

Mineral Analysis, Water-Soluble Vitamins, and pH

The 12 BCS samples plus a composite of the samples were analyzed for minerals by atomic absorption spectroscopy. The composite sample was assayed by Raltech Scientific Services (Hazleton Raltech, Inc., Madison, WI) for water-soluble vitamins. The pH of the samples were determined using a pH meter.

Freezing Point

Approximately 4 ml of BCS, taken from the composite sample, was placed in a test tube (18 × 150 mm). The sample, with a thermocouple (copper-constantan) connected to a voltmeter (Varian G-2000, Walnut Creek, CA) positioned in its center, was then immersed in an acetone bath contained in an insulated calorimeter well. The acetone bath was stirred with a magnetic stirrer and kept at −50° C by adding solid carbon dioxide. The sample was gently shaken (manually) to ensure uniform freezing. After freezing, the sample was moved to a 25° C water bath for melting. A chart (strip-chart recorder) showing EMF vs time was

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obtained in duplicate for each trial. From each chart an inflection point, where the temperature remained constant for a short time, was taken as the freezing point of the sample in question.

Density

A 25-ml graduated cylinder was tared, 25 ml of BCS added, and the cylinder reweighed. Density was calculated from weight and volume (g/ml).

Total Titratable Acidity

Twenty grams of BCS was placed into a 150-ml beaker and diluted with 50 ml of distilled water. The mixture was stirred at room temperature for 30 min, then 0.0948 *M* sodium hydroxide was added to pH 7.0 (determined by pH meter). Results were reported in milliequivalents of base per kilogram of BCS solids.

Specific Heat

ASTM method C351-61 (1980) was modified to measure the specific heats of the BCS samples and that of the composite BCS sample. The equipment used was a specific heat calorimeter (model CS-129, Custom Scientific Instruments, Inc., Whippany, NJ). Specific heat was determined on individual samples at a single temperature. The composite sample was used to determine specific heat vs solids content and temperature. BCS was slowly dehydrated in a low-temperature (38° C), forced-draft oven to 73% solids. The material was then diluted with distilled water to obtain 60 and 20% solids contents.

Thermal Conductivity

The instrument used was a C-Matic thermal conductance tester, model TCHM-DV (Dynatech R/D Corp., Cambridge, MA), which is designed to test low-moisture solids at temperatures between 75 and 400° F. The basis of the determination is a simple, one-dimensional, heat-flow analysis, with the sample sandwiched between a cold plate and a hot plate. The heat flow per unit area from the hot side to the cold is measured. The principle of operation used by this instrument closely resembles that for ASTM specifications C518-76 (1980).

TABLE I
Proximate Analysis and Gross Energy of BCS, Corn, Cane Molasses, and Wood Molasses

Analysis	BCS[a]	Corn[b]	Cane Molasses[c]	Wood Molasses[d]
Total solids, %	44.4 ± 7.4	90.0	66.0	54.1
Protein, % db	8.85 ± 1.14	10.14	5.90	1.1
Carbohydrate, % db[e,f]	74.81 ± 5.88	81.1	84.0	93.8
Fat, % db[f]	1.43 ± 0.30	4.4	0	0.2
Ash, % db	2.54 ± 0.21	2.0	10.10	5.0
Crude fiber, % db[f]	2.09 ± 0.20	1.4	0	0
Gross energy, db (cal/g)	4,073 ± 53	4,393	3,768	6,750

[a] Mean and standard deviation of 12 samples of brewers condensed solubles.
[b] U.S. no. 2 yellow dent corn.
[c] Sugarcane molasses, 48% invert sugar.
[d] Masonex, Masonite Corp., Chicago, IL.
[e] Values for corn, cane, and wood molasses are nitrogen-free extract.
[f] Values for corn, cane, and wood molasses are taken from NAS (1972).

TABLE II
Average Solids and Carbohydrate Components in BCS

Analysis[a]	Results (%)
Average solids	
Total solids	44.4 ± 7.40
Suspended (percent of total solids)	6.9 ± 1.91
Soluble (percent of total solids)	93.1 ± 1.91
Carbohydrate components	
Total carbohydrate	74.8 ± 5.88
Dextrose (DP = 1)	5.8 ± 0.79
Maltose (DP = 2)	32.3 ± 4.19
Maltotriose (DP = 3)	9.9 ± 0.80
Maltotetraose (DP = 4)[b]	3.1
Maltopentaose (DP = 5)[b]	1.3
Maltohexaose (DP = 6)[b]	0
Maltoheptaose (DP = 7)[b]	3.7
$DP \geq 8$[b]	18.6

[a] Mean and standard deviation of 12 samples.
[b] Analysis performed on a single, composite sample of the 12 samples.

A composite BCS sample was freeze-dried, and measurements were made at three temperatures. Thermal conductivities of pure water at different temperatures were obtained from the CRC Handbook of Chemistry and Physics (1973), and thermal conductivities were then computed for BCS at various solid concentrations and temperatures.

Oven-Drying Test

Composite samples of BCS were oven-dehydrated at low temperature to 50% solids, and those samples were then dried in a forced-draft oven at four temperatures (54.4, 65.6, 76.7, and 87.8° C; three replications each) until they browned noticeably. Every few hours, the samples were checked for solids content and browning (color change of BCS). The color change point, which is the solids content of BCS at which the color of the BCS sample darkened, was judged visually by a panel.

Water Activity

The composite sample of BCS was analyzed for water activity vs solids content and temperature. After each sample was placed in the measuring capsule, the temperature of the filled capsule was equilibrated by holding the capsule inside an insulated container. The equilibrium relative humidity (erh) was then measured by a Beckman water activity meter (model SJT-02-08-0, Beckman Instruments, Inc., Cedar Grove, NJ).

Storage-Stability Test

The effects of solids concentration, propionic acid (as a chemical mold inhibitor), and storage temperature on the storage stability of BCS were investigated. The stability of the samples was determined by looking for visual evidence of mold growth or evolution of carbon dioxide. Only five samples (subsamples 7, 12, 14, 17, and 21) out of the total of 12 were examined. Those five represented the range of viscosity and solids observed for all the samples.

For each sample, 12 subsamples were prepared at four propionic acid levels (0, 0.25, 0.50, and 0.75 weight percent, "as is"). The samples were then stored at 21, 26.5, and 32° C.

After a sample had been placed in a mechanical blender and stirred for 5 min, approximately 5 ml of the mixture was placed in an eight-dram vial; the screw cap of the vial was then closed tightly, and the level of BCS (about ½-in. deep) in the vial was marked. Twice daily the samples were checked for any volume change or mold growth. The vials and transfer equipment were sterilized before use.

In another experiment, the effect of shaking the samples on storage stability was examined. An additional three subsamples were taken from each of three samples (7, 17, and 21), using the same propionic acid levels. These samples were shaken continuously at room temperature (about 800° F) on a mechanical shaker.

RESULTS AND DISCUSSION

Composition

Table I gives the mean values and standard deviations for proximate analysis and gross energy of the 12 BCS samples. The average values for corn, cane molasses, and wood molasses are listed for comparison. The carbohydrate content of BCS was found to be approximately 75% by the phenol-sulfuric acid method using glucose as a reference standard. When computed by difference, however, the carbohydrate content of BCS was 87%, in agreement with the other calculated carbohydrate percentages given in Table I. The disparity in carbohydrate values deserves further investigation.

Gross energies were lower in BCS and cane molasses than in corn or wood molasses because of differences in composition. BCS and cane molasses contain mostly short-chain carbohydrates, whereas corn is predominantly starch. Molasses contains more ash than BCS, which accounts for its relatively lower energy content. The organic matter in wood molasses (Masonex) is mostly hemicellulose. Masonex also contains phenolics, which increase its gross energy content.

Table II shows that most of the solids (93%) in BCS were in a soluble form. In general, when total solids in BCS were higher, suspended solids were lower. The main carbohydrate components in BCS are also given. Maltose accounted for almost 45% of the carbohydrate, maltotriose constituted 13%, and maltodextrins of chain length greater than 7 constituted almost 19%.

The essential and nonessential amino acids in BCS and corn are given in Table III. The balance of essential amino acids in BCS was better than that of corn for monogastric animals. BCS contained 1.4–1.5 times the levels lysine and tryptophan, which are the first and second limiting amino acids in corn. The very high level of leucine in corn was halved so that its amount in BCS was nearer to that of the ideal reference protein.

Results of the mineral analyses of BCS are given in Tables IV and V. In general, BCS surpassed corn and wood molasses as a source of minerals, especially phosphorus and iron. BCS, however, is not nearly so rich a source for most minerals as is cane molasses. Heavy metals in BCS were very low; they occurred in the parts-per-billion range (Table V). Heavy metals in BCS generally were lower than in cane or black-strap molasses.

Table VI contrasts the amounts of water-soluble vitamins in BCS with those in corn and molasses. Except for thiamine, pyridoxine, and pantothenic acid, BCS compared favorably with corn and molasses as a source of water-soluble vitamins.

Selected Properties

Several selected properties of BCS are given in Table VII. BCS was acidic with an average pH of 4.14, and a titratable acidity of 208 meq base/kg of solids. The freezing point of BCS averaged −8.6° C and was found to vary with solids content according to the equation

$$Y = -0.00133\ X^{2.3316},$$

where Y is the freezing point (° C), and X is the solids content

TABLE III
Amino Acids in BCS and Corn

Amino Acid[a]	BCS[b]	Corn[b]
Essential		
Threonine	3.34 ± 0.14	3.44
Valine	4.35 ± 0.23	3.10
Methionine	1.45 ± 0.14	1.85
Isoleucine	2.66 ± 0.17	1.92
Leucine	5.93 ± 0.27	11.89
Phenylalanine	4.26 ± 0.16	4.35
Histidine	4.71 ± 0.37	3.98
Lysine	3.28 ± 0.28	2.32
Arginine	4.80 ± 0.66	4.78
Tryptophan[c]	1.50 ± 0.61	0.99
Nonessential		
Aspartic acid	7.98 ± 0.33	7.02
Serine	4.33 ± 0.17	5.33
Glutamic acid	20.52 ± 1.21	19.77
Proline	12.33 ± 1.01	9.44
Glycine	5.08 ± 0.22	4.18
Alanine	6.79 ± 0.43	9.16
Half cystine	1.07 ± 0.16	1.37
Tyrosine	3.45 ± 0.34	3.52
Ammonia	2.21 ± 0.40	1.59

[a] Essentiality is based on the growing pig (20–35 kg).
[b] Brewers condensed solubles. Determined at Kansas State University. Units are in g of amino acid/100 g of protein (corrected to 100% recovery). The values are the means and standard deviations of assays of the 12 samples.
[c] Tryptophan was determined by separate analysis.

TABLE IV
Macro- and Micro-Minerals[a] in BCS, Corn, Molasses, and Wood Molasses

Mineral	BCS[b]	Corn[c]	Cane Molasses[c]	Wood Molasses[c]
Macro				
Calcium, ppm	1,539 ± 206	200	10,500	23,300
Phosphorus, %	0.382 ± 0.022	0.29	0.11	0.05
Nitrogen, %	1.403 ± 0.212	1.62	0.18	0.16
Sodium, ppm	1,349 ± 248	100	2,000	500
Potassium, ppm	1,097 ± 72	3,300	40,200	600
Sulfur, ppm[d]	437	900	4,600	500
Chloride, ppm[d]	631	449	37,200	2,000
Magnesium, ppm	1,456 ± 121	1,200	4,700	1,100
Micro				
Iron, ppm	85.0 ± 22.4	20	240	ND[e]
Copper, ppm	3.07 ± 1.76	4.2	80.2	ND
Cobalt, ppm	0.03	0.02	1.22	ND
Manganese, ppm	13.55 ± 2.50	6.4	57.2	ND
Zinc, ppm[d]	12.56 ± 2.64	10	4.3-13.6	ND
Iodine, ppm	<0.025	···	···	ND
Selenium, ppm[d]	0.04	0.04	···	ND

[a] All values are on a dry matter basis.
[b] All values except sulfur, chloride, cobalt, iodine, and selenium are means and standard deviations of assays on the 12 samples. Sulfur, chloride, cobalt, iodine, and selenium were determined on a composite of all 12 samples.
[c] Values are from NAS (1972) unless otherwise specified: corn, dent yellow U.S. #2; sugarcane molasses, 48% invert sugar. The only micromineral value available for wood molasses (Masonex) was for manganese, and the level is 20.3 ppm.
[d] Values are from NRC (1979). Values for molasses and for major American sources of cane are from Morriss and Nicol (1974).
[e] Not determined.

TABLE V
Heavy Metals in BCS and Cane Molasses

Metal (ppm)[a]	BCS[b]	Cane Molasses KSU Sample[c]	Black-Strap East-Coast Sample[c]
Arsenic	<0.025	<0.014	<0.14
Lead	0.044	2.20	0.55–1.1
Mercury	<0.020	0.011	<0.7
Cadmium	0.020	<0.140	0.04–0.08

[a] All values are on a dry matter basis.
[b] All values were determined on a composite of all 12 samples.
[c] Kansas State University sample from Westway Trading Co., Industrial Molasses Div., Minneapolis, MN. Data on east-coast sample from Raymond Moroz, private communication, 1982.

TABLE VI
Average Amounts[a] of Water-Soluble Vitamins in a BCS Composite Sample, Corn, and Molasses

Vitamin (ppm)	BCS[b]	Corn[c]	Cane Molasses[d]
Thiamine	0.58	4.0	1.3
Riboflavin	1.28	1.0	3.8
Niacin	34.53	23	39.8
Pyridoxine[e]	1.46	7	2.6–5.0
B_{12}	1.12	0	···
Biotin[f]	0.043	0.124	0.946
Choline	650	537	1,189
Folic acid[e]	0.24	0.2	0.04
Pantothenic acid	1.52	5.0	51.8

[a] All values are on a dry matter basis.
[b] All values were determined on a composite of all 12 samples.
[c] Values were obtained for corn, yellow dent, from Inglett (1970).
[d] Values were obtained for sugarcane molasses, 48% invert sugar, from NAS (1972).
[e] Values for molasses are from United Molasses Trading Co., Ltd. (1971).
[f] Values for corn and molasses are from NRC (1979).

expressed in percentage. The regression coefficient (r) computed for the expression was 0.959.

The density of BCS exhibited a linear relationship with solids content. The equation relating density (ρ) to solids content, which gave a regression coefficient (r) of 0.997, is

$$\rho = (1 + 0.4134\ X)\ (10^3),$$

where ρ is the density (kg/m^3), and X is the solids content in decimal form.

The specific heat of BCS gave a mean value of 3.093 J/kg-K. A negative linear relationship ($r = -0.911$) was derived between solids content and specific heat for the 12 BCS samples. The equation is

$$Cp = -0.02899\ X + 4.3804,$$

where Cp is the specific heat in J/kg-K, and X is the solids content in percent. Attempts were made to determine a relationship between specific heat and temperature. Within the temperature range of 40–80°C, the specific heat of BCS did not vary significantly, but remained as defined by the above equation.

The average value for thermal conductivity was found to be 0.349 W/m-K. No mathematical relationship could be derived between the temperature of BCS (30–55°C) and its thermal conductivity. However, a relationship was derived between thermal conductivity and solids content as follows:

$$k = -0.2342\ X + 0.6343,$$

where k is thermal conductivity in W/m-K, and X is the solids content in decimal form.

TABLE VII
Selected Properties of BCS

Property	Value[a]
pH	4.14 ± 0.222
Freezing point (° C)	−8.6 ± 2.75
Density (kg/m^3)	1.196 × 10^3
Total titratable acidity (meq/kg solid)	208 ± 42.2
Specific heat (J/kg-K)	3.093 ± 0.237
Thermal conductivity (W/m-K) (dry solids)	0.349 ± 0.027

[a] Values, except density, are means and standard deviations of assays performed on the 12 samples. The value for density was a determination of a composite of all 12 samples containing 44% total solids.

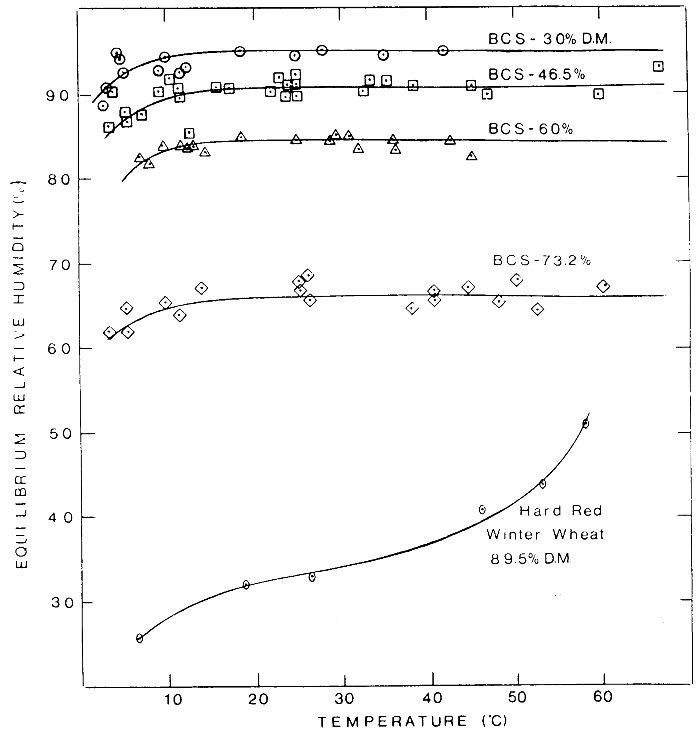

Fig. 1. Equilibrium relative humidity for a composite sample of brewers condensed solubles at various solids contents.

Surprisingly, the water activity (Fig. 1) of BCS did not change as temperature was increased from 15 to 60°C. Between those temperatures, water activity was found to vary with solids content as follows:

$$erh = (3.981\ X - 6.003\ X^2 + 3.202\ X^3) \times 100,$$

where erh is the equilibrium relative humidity in percent, and X is the moisture content in decimal form.

Five of the BCS samples examined for microbiological stability had a wide variation in solids content and viscosity. During three months of the study, two of the five samples, both of which had low solids and low viscosity, began to mold and ferment. However, addition of as little as 0.25% propionic acid stabilized all samples for the three-month period. Increasing the storage temperature to 32°C did not affect the stability of the treated samples.

In an oven-drying test we identified the critical concentrations at which BCS begins to darken during dehydration at several different drying temperatures. The critical solids contents and drying periods required for each temperature were as follows: 54°C, 86.1% solids, 168 hr; 66°C, 83.4% solids, 45 hr; 77°C, 81.3% solids, 8 hr; and 88°C, 81.4% solids, 4 hr.

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