COCONUT SHELLS AS AN INDUSTRIAL RAW MATERIAL

I. COMPOSITION OF SHELLS

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THE object of these articles is not so much to report new observations (though the preliminary results of some unpublished work are included) as to review the properties of coconut shells and to examine their status as a potentially valuable raw material.

Composition

(*i*) *Moisture*.—The moisture content of shells varies considerably with conditions and with maturity. Under average conditions air-dried mature shells contain 6 to 9 per cent. of moisture[1,2] and thus retain less moisture than most woods. This is an important point in connection with dry distillation (see subsequent article). All analytical figures quoted in the following discussion are given as percentages of dry material, unless otherwise stated.

(*ii*) *Ash*.—Figures ranging from 0·23 to 1·425 per cent. have been recorded; recent references give values based on dry weight, but in the older citations it is not usually clear whether or not the results have been so corrected. The following is a selection of analytical figures from the literature:—

shell charcoal is required by some specifications (see second article) to contain not above 2·0 per cent. by weight of the original shells; this implies a maximum of 0·67 per cent. ash on the latter and the writer has, in the course of examining many samples of charcoal, never found this limit exceeded with uncontaminated samples. Potash is clearly the principal constituent of the ash. The salts will largely be present as carbonates, but phosphate, sulphate and silicate also occur, as well as chloride. It is curious that chloride estimations have not been recorded; the writer's (unpublished) analyses of charcoal samples indicate the presence of 1 to 2 per cent. of Cl[1] in the ash.

About 90 per cent. of the ash is water-soluble, and the present writer[2] has also shown that most of the potash is extracted from the powdered shells by hot water.

The ash content is comparable with that of most woods; the large proportion of soluble ash is an advantage in the preparation of activated charcoal, since it is easily removed.

Georgi and Gunn Ley Teik[15] report the

Authors	Reference	Date	% Ash	As percent. of ash							
				K_2O	Na_2O	CaO	MgO	Fe_2O_3 + Al_2O_3	P_2O_5	SO_3	SO_2
Fleck *et alii.* ..	1	1937	0·23	—	—	—	—	—	—	—	—
Bachofen ..	12	1899	0·29	45·01	15·42	6·26	1·32	1·39	4·64	5·75	4·64
Phillips and Goss ..	4	1940	0·55	—	—	—	—	—	—	—	—
Child and Ramanathan ..	2	1938	0·61	—	—	—	—	—	—	—	—
Georgi .	5	1941	0·69	52·20	—	—	—	—	—	—	—
Norris (quoted by Sampson) ..	3	1923	1·10	31·6	—	2·97	3·87	—	5·32	—	—
Lépine (quoted by Copeland &c.)	13	(1861)	1·41	*	—	*	—	—	*	—	—
Fesca ..	16	1904	1·425	30·0†	—	2·32†	1·12†	—	5·00†	—	—

* 86·94 per cent. of "salts of K"; 2·18 per cent. of calcium phosphate; "salts of Ca" 6·53.

† Calculated from the figures given in Preuss (*loc. cit.*) as the percentages on the original shell, assuming an ash content of 1·425%.

Doubtless the percentage and composition of the ash vary with soil and climatic conditions, habitat and variety of palm; thus the nuts examined by Bachofen and by Child were of Ceylon origin; by Norris from Madras Presidency; by Georgi from Malaya; and by Phillips and by Fleck possibly from the Philippine Islands. Maturity of the nut also affects the composition of its component parts, and Copeland (*loc. cit.*, p. 174) remarks that "Bachofen's nut cannot have been thoroughly ripe"; there seems, however, little reason for this statement.

The figures of Bachofen and the still older results of Lépine have been extensively quoted in the literature. Great confidence can hardly be reposed in those of Lépine, which (see Bibliography) appear to date back at least to 1861, but those of Bachofen are useful, pending the collection of further data, in that they give at least some idea of minor constituents.

In the writer's experience in Ceylon, an ash content of 0·6 per cent. is usual. Coconut

following average figures for eight lots of shells averaging 20·2 per cent. moisture (*i.e.*, not air-dried but as collected): K_2O 0·364, CaO 0·009, MgO 0·014, P_2O_5 0·035. They do not, however, state the actual ash contents, so that their figures cannot be collated with the above table; from inspection of the figures it looks as though the ash content would have been considerably higher than 0·6 per cent.

(*iii*) *Organic Constituents*.—An early analysis is that of W. L. Winton[6] in 1901, who employed the ordinary methods of Food and Drug examination for the detection of powdered coconut shell in species which adulteration he stated to be a common practice in the United States. His figures are not now of particular interest; a value of 56·19 per cent. was recorded for "crude fibre", but this is now known to have little definite relation to the structural constituents of the original material. Curious figures of Brandes, quoted by Hunger[14] are of little value.

More adequate proximate analyses have been published by Fleck[1] (1937) by the present writer[2] (1938), and by Phillips[4] (1940). The original papers should be consulted for details; the chemistry of cell-wall substances is in an active state of development and methods of analysis are still somewhat empirical. However, the three sets of observations quoted are in fair agreement over the main features of the composition of coconut shells.

(*a*) *Solvent Extractives.*—Only small quantities of material are extractable by non-hydroxylic solvents, 0·19 per cent. by ether,[1] and 0·27 per cent. by benzene.[2] Alcohol has been found to extract 2·51 per cent.[2] and a 1:2 alcohol-benzene mixture 4·56 per cent.[4] The manner in which coconut shells burn has given rise to the supposition that they contain considerable quantities of oily or resinous matter; this is seen not to be the case. The nature of the solvent extracts has not been examined, but the alcohol extract presumably contains some tannin matter.

Cold water has been reported to extract 1·43 per cent.[1] and 0·20 per cent.,[2] and hot water 2·67,[1] 3·57[2] and 2·76.[3] 1 per cent. caustic soda removes 20·53 per cent. of material[1] or 18·80 per cent.;[2] and 1 per cent. hydrochloric acid, 29·69 per cent. These figures are of limited theoretical value, since the alkali- or acid-soluble fractions are not clearly defined; the former, for example, includes part of the lignin and of the polyuronide and cellulosan fractions.

(*b*) *Nitrogen.*—Georgi and Gunn Ley Teik[15] give the analysis of eight samples as 0·073 to 0·090 per cent. (average 0·081 per cent.) for shells having a moisture content of 20·2 per cent. (not air-dried but fresh collected). This corresponds to an average per cent. nitrogen on dry weight of 0·10 per cent. and agrees well with the 0·11 per cent. reported by Phillips.[4]

A somewhat higher figure, 0·156 per cent. is given by Fesca.[16] The nitrogen seems to be largely associated with the lignin fraction (see below).

(*c*) Lignin.—The percentages of lignin reported are 33·30,[1] 36·51[2] and 27·26 per cent.[3] Methods of determination were all different and there may, of course, have been some natural variation between the samples examined. In the writer's opinion a figure of 32·0 per cent. is, probably, fairly near the true value.

Phillips gives a figure of 0·29 for the percentage of nitrogen in the lignin; this accounts for over 70 per cent. of the total nitrogen (see above).

Methoxyl.—The methoxyl content of shells has been reported as 5·39[1] and 5·84 per cent.[3] According to Phillips,[3] the lignin fraction contains 16·17 per cent. methoxyl or 16·46 per cent., calculated on the nitrogen and ash-free lignin. This accounts for 4·41 per cent. of the original. It does not, however, follow that the balance of about 1 per cent. methoxyl is associated with the non-lignin constituents of the shells, since it is by no means certain that there is no loss of methoxyl during the isolation of the lignin by strong acid treatment.

The lignin content of the shells is higher than that of most woods. Further reference is made particularly to the methoxyl content in the discussion of the distillation product of shells in a subsequent article.

(*d*) *Total Pentosans.*—Both Fleck[1] and the present writer[2] estimated pentosans by the method of Schorger, and obtained similar figures, *viz.*, 30·28 and 29·27 per cent. respectively. These figures were not corrected for the presence of polyuronides. Phillips[3] determined uronic acid anhydrides as 3·82 per cent. and used an empirical formula to give a correction for the amount of furfurldehyde derived from the uronic acids; this correction came to 1·42 per cent. calculated as pentosans, and his so corrected "total pentosans" figure to 30·14 per cent.

The estimates of "total pentosans" by the three sets of workers are thus reasonably concordant. The percentage is considerably higher than in most woods and is the highest recorded for all nut-shells so far examined,[7,8,4]

No further quantitative details are available regarding the nature of the pentosans, but as long ago as 1895 Tromp de Haas and Tollens[11] obtained a "satisfactorily yield" of crystalline xylose by hydrolysis of coconut shells with 4 per cent. sulphuric and stated that this appeared to be the only product of the hydrolysis. The residue gave dextrose on further hydrolysis with stronger acid.

(*e*) *Cellulose.*—Published estimates of "cellulose" differ considerably and it is obvious that this is largely due to the methods of estimation and that the various workers were not dealing with similar "cellulose" fractions. Phillips'[3] use of the method of Kürschner and Hanak[9] seems to imply his opinion that the Cross and Bevan method or modification thereof as used by Fleck[1] and by the present writer[2] is less reliable for resistant materials like coconut shells. The wide discrepancies between the recorded percentages of "crude cellulose" become less serious when adjustment is made for the pentosan content. All the three workers determined the furfurldehyde yield of their "crude cellulose" and calculated the pentosan content in the usual way based on Krober's work:

	Fleck (1)	Child (2)	Phillips (3)
% Crude Cellulose ..	44·98	53·06	33·52
,, Pentosan in Cellulose	17·67	20·54	5·26
,, Cellulose ..	27·31	32·52	28·26

It would appear, therefore, that the "crude cellulose of each worker differed materially only in that the respective methods of treatment had removed more or less of the pentosan fraction.

No further examination of the nature of the "cellulose" has been carried out, except that Fleck determined the arbitrary "Hydrolysis No.", *i.e.*, *the* percentage loss in weight after hydrolysis with 15 per cent. sulphuric acid, which he found to be 35·85. It may be noted that this is not markedly different from his figure for the pentosan content of the cellulose. Fleck also determined the "holocellulose" fraction by the method of Van Beckum and Ritter;[10] this fraction, 61·0 per cent., purports to represent the entire non-lignin constituents of the cell-wall, and indeed does accord reasonably well with an estimate of 32·0 per cent. for lignin, allowing also for ash and extractives.

Further examination of "cellulose" fractions obtained in various ways seem to be desirable and a critical examination of methods of preparation. It seems safe to say, however, that the cellulose content of coconut shells is lower than that of most woods.

Boswell[8] noted that the cellulose separated from Brazil nut-shells was obtained as a hard mass whatever method of drying was used, and the writer has made a similar observation on cellulose derived from coconut shells, which was always obtained as a hard horny mass.

(iv) *Discussion.*—Qualitatively, coconut shells resemble, in composition, the hard woods, but they have higher contents of lignin, total pentosans and pentosan in cellulose, and lower contents of cellulose. The methoxyl content does not differ greatly from those of many woods. The nature of the products obtained by dry distillation (described in a subsequent article) show considerable quantitative differences from those of woods, and it is likely that these differences point to features in the composition of the raw material not indicated by existing analytical methods. It is believed that further investigation of the various fractions—lignin, "cellulose", pentosan, etc.,—would yield results of interest in the chemistry of cell-wall substances. This is probably also true of other nut-shells, few of which have been studied (see Refs. 7, 8, 4), but which present several novel points of interest.

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INDIA'S POST-WAR INDUSTRY

THE question of capital re-equipment of Indian industry was raised by Sir Azizul Haque, Commerce Member, in his opening address to the meeting of the Post-War Reconstruction Policy Committee on Trade and Industry, on Thursday, the 21st October 1943. "The Government of India", he said, "have by no means lost sight of this aspect of the problem which the continuation of the war, with a consequent continuation of excessive wear and tear on plant, and increased difficulty of replacement, has made more acute. In so far as those machineries and plants have to be imported from abroad, I am convinced that no time should be lost in making an aggregate estimate of India's total post-war requirements. It will be necessary, without any avoidable delay, that the Governments or organisations of exporting countries must know the approximate extent of India's post-war requirements."

All industries are asked to take up this question as soon as possible so that the Government of India might take the necessary steps in that direction. It was the duty of the Government to assist new industry and new enterprise, but the Government must also look to trade and industry to state what were likely to be the scope and prospects of such new industries. "In the exigencies of war conditions industries are necessarily organised, mobilised, and shaped to meet the exigencies of war production, but it is time for us to try to plan the future, assess the place of these war industries in post-war conditions, and give our thoughts to other human and social aspects of life, and conditions of industrial labour so that men may not decay with a mere accumulation of wealth."

Therefore, Sir Azizul added, the Government were submitting to industries for their consideration a draft questionnaire which would give them the information they sought. He also emphasised that the questionnaire was a purely provisional document, and if the industries thought that some other method of getting the necessary information was to be preferred, they could give their views. The Committee decided the terms of a questionnaire to be addressed to industries to elicit factual data on which definite plans for post-war developments could be based. It also discussed India's trade policy in the post-war period, and the future of India's industrial policy.