THE DESTRUCTIVE DISTILLATION OF COCONUT SHELLS

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WHEN wood and similar substances are heated in a closed space in the absence of air, they are decomposed with the formation of charcoal and volatile products. Coconut shells have a composition qualitatively similar to that of hard woods (Cf. Fleck, Van Beckum and Ritter, 1937 ; Child and Ramanathan, 1938).

In Ceylon, coconut shells are largely employed for the production of charcoal, export figures of this product since 1933 being as follows :—

Year.	Amount. (tons.)	Value. Rs.	Value per ton. Rs.
1933	2,019	90,541	44·85
1934	6,234	350,996	56·30
1935	7,667	365,608	47·68
1936	6,751	377,137	55·86
1937	13,455	977,708	72·66
1938	10,997	823,781	74·91

This charcoal is produced by the time-honoured method of carbonizing the shells in pits and no attempt is made to recover by-products. Roughly 20,000 shells are required to produce a ton of charcoal ; there is, in addition to the exports, a limited local consumption of charcoal for fuel, in gas engines, &c., so that it may be estimated that in 1937 and 1938, about 250 to 300 million shells each year were burned for charcoal.

Since the outbreak of war there has been experienced in Ceylon a shortage of acetic and formic acids for rubber coagulation, with inflated prices for these commodities. This may be only a temporary phase, but the question has been raised whether acetic acid could not be recovered from the by-producst of coconut shell distillation.

It is the object of the present article to review what is known of the yields and composition of the products from the dry distillation of coconut shells, and thus to provide data upon which may be based consideration of their possible economic development.

PRIMARY PRODUCTS OF DESTRUCTIVE DISTILLATION

The primary products of distillation are *charcoal*, which remains in the retort or oven in which the shells are heated; *pyroligneous liquor* and *settled tar*, which distil over and are condensed in suitable water or air cooled condensers; and *uncondensable gases.*

The course of distillation is somewhat as follows: at the commencement of heating, the first action is to dry out the contained moisture of the shells (about 9–10 per cent.) and the first distillates are mostly condensed water; thereafter the main reactions set in with the formation of large quantities of gas and the liquid distillate contains acetic acid, methyl alcohol and some tar; the reaction becomes exothermic at about 290°C, *i.e.*, continue without the necessity of external heat. When this stage is over, with continued external heating tarry matter predominates in the distillate.

Yields of Primary Products.

Several studies on shells have been reported and Table I. shows the results recorded of the yields of the primary products. Literature references to the table will be found at the end of this article. Columns 6 and 7 refer to commercial trials carried out in 1934 respectively by Messrs. H and T. Danks (Netherton), Ltd., and by Messrs. Low Temperature Carbonisation, Ltd., on behalf of Messrs. Lee Hedges & Co., Colombo, and are included by courtesy of the latter firm.

Ramachandran (1938) has described experiments on the effect of adding certain chemicals to the shells before distillation, reporting that zinc and magnesium salts gave an increased yield of pyroligneous liquor, whilst aluminium salts reduce the yield of pyroligneous liquor but slightly increase the yield of settled tar. In view of the considerable variation of the results given by different observers, these statements probably need confirmation. It is possible that shells from different sources behave differently, but it is the writer's opinion that the main causes of variation are (i.) differences in the moisture content of the shells and (ii.) lack of standardization of distillation conditions. Thus the high charcoal figures and low liquor and tar percentages reported by Georgi and Buckley (column 4) probably point to insufficient heating; the low charcoal and high tar figures of the commercial trial by Messrs. Low Temperature Carbonisation, Ltd. (column 7) indicate thorough carbonisation; whilst the figures of the writer (column 5) are known to have been due to good heating of the retort but inefficient condensation of the distillate.

In spite of this variation in the reported results, they are in sufficient accord to show what yields should be obtainable under good conditions of distillation and the general averages (excluding the extreme figures) work out approximately at :—

Charcoal	34 lb.	from 100 lb. of shells.
Pyroligneous acid	40 lb.	
Settled Tar	6 lb.	
Gas	20 lb.	

Acetic acid under good conditions should reach 12·5 per cent. in the pyroligneous liquor, or 5 per cent. of the weight of the shells. That is to say, since 250–300 million shells weigh about 36 to 45,000 tons, the equivalent of some 2,000 tons of glacial acetic acid is annually burnt off into the air in the manufacture of charcoal in Ceylon.

The annual requirements of the Ceylon rubber industry of acetic and formic acid together do not greatly exceed 500 tons.

COMPOSITION OF THE PRIMARY PRODUCTS

The distillate separates into two layers, the top known as "pyroligneous liquor" and the latter as "settled tar". The settled tar does not represent all the tarry substances present, parts of which remain in solution in the pyroligneous acid and are known as "dissolved tar".

Pyroligneous Acid (the word "pyroligneous" simply indicates "derived from wood by a process of heat"), is by no means a simple chemical substance, but a complex mixture of a large number of compounds. The actual composition varies with conditions of distillation and with the raw material used. The principal constituent is, however, acetic acid, and "pyroligneous liquor" or "pyroligneous acid" may be regarded as an impure dilute acetic acid contaminated with other compounds. It is a dark, reddish-coloured liquid with a strong, smoky smell. As will be seen from the Table, the acetic acid content may vary between about 7 and about 15 per cent. but with dry shells and satisfactory distillation at least 10 per cent. should be obtained, and if the weaker first distillates be rejected, at least 12·5 per cent.

The other constituent of importance is "wood naphtha," a mixture of methyl alcohol and acetone. The percentage has been reported as 2½–3 per cent. in the liquor, or 1–1·2 per cent. on the original shells. (Wells, 1917; Sudborough, 1920).

Settled Tar.—The division of constituents into those present in pyroligneous liquor and in the settled tar is, of course, only approximate, since any of the main constituents of one may be found in small quantities in the other. The settled tar, for example, contains some acetic acid.

The tar is a very complex mixture. There is nothing like a complete analysis on record, and there is very much more variation between the tar from various sources than in the pyroligneous liquor. Thus coconut shell tar differs considerably in composition from (say) beech wood tar, and is dealt with later.

Charcoal contains the non-volatile products. It consists mainly of amorphous carbon, but retains adsorbed some of the volatile products of carbonization and also contains the inorganic (ash) constituents of the shells. A separate account of the subject of coconut shell charcoal will be given in a separate article and further details are accordingly not given here.

Gas.—The gas evolved contains mostly carbon dioxide and monoxide, but the actual composition will vary considerably with conditions of distillation. The only available report on the gas from coconut shells (column 7) gives the following details :—

Yield—5,144 cu. ft. per ton of shells (16·4 per cent.)

Calorific value—396 B.T.U./cu. ft.

Sp. gravity—0·9336.

Therms of gas per ton of shells carbonized—20·37.

COMMERCIAL UTILIZATION OF THE PRODUCTS

Coconut shells compare very favourably with most woods as raw materials for distillation, particularly in two respects. The moisture content of air-dried shells is low (not more than 10 per cent.), and the yields of acetic acid are extremely good.

Treatment of Pyroligneous Acid.—In the wood distillation industry, pyroligneous acid is usually redistilled to separate it from dissolved tar. The distilled pyroligneous acid is neutralized with lime and partially distilled to recover the " wood naphtha," the latter being then purified by suitable means. The neutralized solution remaining is evaporated to dryness leaving acetate of lime known commercially as " grey acetate."

From " grey acetate", acetic acid is obtained by treatment with sulphuric acid, and purified by suitable rectification.

The latter operations are matters of specialized technique, and it may be said at once that, in the writer's opinion, it would not be practicable to undertake them in Ceylon.

It should also be made clear at this point that it is not possible to concentrate acetic acid from dilute solutions such as pyroligneous acid by simple distillation. The boiling points of water (100°C) and of acetic acid (118°C) are fairly close together, and no constant boiling mixture are formed, as in the case of alcohol.

Numerous attempts have been made by industrial chemists for many years to concentrate acetic acid from pyroligneous acid without going through the intermediate stage of acetate of lime. Solvent extraction processes have been the most successful of these, of which, among others, are processes using ethyl ether (Brewster process), *iso* propyl ether (modified Brewster process) and wood oil (Suida process). A description of these is given by Partridge (1931).

All such processes involve specialized plant and technique. It may, therefore, be considered that the production of glacial acetic acid, or even 50 per cent. acetic acid, cannot possibly be contemplated in Ceylon at the present stage of development.

All that could be contemplated is the possible purification of pyroligneous acid to provide a reasonably pure dilute acetic acid of about 10–15 per cent. strength which would be suitable for rubber coagulation; and also, since lime is a local product, the production of a certain amount of "grey acetate." Both of these are technically possible, since they involve fairly simple plant and do not require imported chemicals. The difficulties are not technical but economic.

The writer's experiments using a pyroligneous acid of 9·33 per cent. w/v acid content (as acetic) show that, by the addition of 30 per cent. by weight of crude salt to raise the boiling point, it is possible by simple distillation to effect considerable purification and some concentration. A number of runs showed that the first 5 per cent. approximately of the distillate contained most of the "wood naphtha"; the next 50 per cent. was a colourless distillate averaging 11·1 per cent. w/v acidity as acetic.

It is still, however, by no means pure dilute acetic acid. Besides acetic acid, the redistilled liquor contained some formic acid and dissolved phenols. The former amounted to 0·43 per cent. w/v and the latter (determined by chloroform extraction) to 2·36 per cent. w/v. Furfural was detected qualitatively. The presence of formic acid would not be a disadvantage in rubber coagulation, but coagulation and vulcanization tests on rubber prepared by the use of the material are necessary to ascertain whether phenols, furfural and other compounds have any deleterious effect.

Further experiments are in progress to see whether better recovery is possible, and the Director, Rubber Research Scheme, has agreed to carry out the necessary test coagulations and vulcanizations.

Reference might be made here to the patent of E. C. R. Marks (1915) which claims “ a process for coagulating latex characterized in this that the gases obtained by the destructive distillation of wood, in suitable retorts, or the like, after removal of the tar from the gases, are employed for treating the latex”.

It would probably not be worth while in Ceylon attempting to recover methyl alcohol or even crude “ wood naphtha ”. There is no local demand for the product, and the recovery is in any case more difficult in tropical than in temperate climates.

Grey Acetate.—In 1916 (Bull. Imp. Inst., *loc. cit.*), samples of grey acetate were prepared in Ceylon, and the Imperial Institute reported on them as follows :—

> “ It consisted of a coarse powder, pale grey in colour, and had a tarry odour. Its solution in water was of dark-brown colour.
>
> On analysis the sample gave the following results :—
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> | | |
> |---|---|
> | Moisture .. .. .. | 3·50 |
> | Calcium acetate .. .. .. | 83·60 |
> | Sulphates expressed as calcium sulphate .. .. | 0·60 |
> | Carbonates expressed as calcium carbonate .. | 0·08 |
> | Total ash .. .. .. | 32·20 |
> | Matter insoluble in water .. .. .. | 1·20 |
> | Free lime
Calcium formate
Sulphites .. .. .. | Nil |
>
> This sample corresponds in quality with commercial ‘ grey acetate of lime’, which usually contains 80 per cent. of acetate of lime. The amount of tarry matter is not excessive.”

At that time grey acetate had increased in price from £8 per ton in July, 1914, to £38 a ton, and inquiries were received from the United Kingdom whether supplies were likely to be available for export from Ceylon. Grey acetate, as mentioned above, is used for the production of glacial acetic acid, and it is also a source of acetone, a solvent employed in the manufacture of cordite and for other purposes.

Coconut Shell Tar

M. K. Narasimhan (1920) has reported a fairly comprehensive examination of the tar from coconut shells. Wells (1917) had previously given the results of distillation.

A sample of 1,586 grammes examined by the writer gave the following boiling point figures on distillation :—

	Weight in grammes.	Per cwt.	Per cwt. excluding (*a*) and losses.
B. Pt. up to 120° 268 gm.	187(*a*)	11·8	—
	61	3·8	4·4
120°–200°	312	19·7	22·5
200°–240°	435	27·4	31·3
240°–260°	95	6·0	6·8
Residue	485	30·6	34·9
Experimental losses	11	0·7	—
	1,586	100·0	99·9

(*a*) was a aqueous layer containing 10·6 per cent. w/v acetic acid. These figures are in general agreement with those of Wells and of Narasimhan. Wells found that 60·5 per cent. distilled below 250°C; Narasimhan that 69 per cent. distilled below 260°C compared with 69·4 per cent. found by the writer. This percentage of volatile substance is high compared with most wood tars.

The writer confirmed the presence of 5 per cent. of phenol, which was identified as the benzoate m.p. 68°C; and also found that the guaiacol content (unlike that of beech wood tar) was very low.

Narasimhan (*loc. cit.*) described the residue after distilling off the substances volatile below 260° as a hard brittle pitch. The writer did not find this to be the case. Even after further distillation *in vacuo* at 0·04 mm., by which it was resolved to 20·4 per cent. of the original tar, the residue remained a viscous liquid, which did not harden when exposed to the air for eight months.

A crude shell oil (*poḷ-katu teḷ*) is used locally and in other coconut-growing countries as a rough and ready antiseptic. Its preparation using rudimentary apparatus is described by Kidavu and Nambiyar (1927). Compare also Wray (Perak Museum Notes, 1897, **2**, p. 35).

Cooke (1936), in his bulletin on the Coconut Industry in the Philippines, states that " it is understood that when coconut shell is steam distilled an oil of medicinal use, having a commercial value in America, is obtained ". The writer (1936) was unable to obtain any such oil when finely-ground shells were steam distilled at ordinary pressure, and considers that the reference is possibly to steam distillation of shell tar.

The products from coconut shell tar would, in any case, repay further examination, particularly the creosote fraction.

Table I.—Yields of Primary Products from Dry Distillation of Coconut Shells.
(Percentages by Weight).

	Bull. Imp. Inst. (1916)	Wells. (1917)	Sudborough. (1920)	Georgi. (1929)	C.R.S. (1934)	Danks & Co. (1934)	L.T.C., Ltd. (1934)	Ramachandran. (1938)	
	1.	2.	3.	4.	5.	6.	7.	8.	9.
Charcoal ..	—	32 ·5	38 ·3	49 ·0	30 ·0	40 ·6	29 ·2	37 ·2	35 ·1
Pyroligneous acid	—	41 ·3	35 ·4	29 ·9*	38 ·9		41 ·3	39 ·4	41 ·0
		3 ·2				37·5			
Tar	—	6 ·9	6 ·3	2 ·9*	4 ·6		10 ·7	5 ·4	7 ·2
Loss as Gas ..	—	16 ·2	20 ·0	18 ·2	26 ·5	21 ·9	16 ·4 (measured)	18 ·0	16 ·7
Acetic acid % in Pyroligneous acid	8 ·12	—	—	15 ·8	9 ·33	—	—	14 ·0	7 ·3
Acetic Acid % on shells	—	6 ·3	6 ·9	4 ·66	3 ·63	—	—	5 ·5	3 ·0
Source of shells	(Ceylon)	(Philippine Islands)	(S.India)	(Malaya)	(Ceylon)	(Ceylon)	(Ceylon)	(Bangalore)	(Trivandrum)

*Calculated from values given on basis of Sp. Gr. of pyroligneous acid 1·04 and tar 1·1.

Cf. Also A.I. de Leon and R. O. R. Reyes. " Utilization of some Agricultural Waste Products. I. Destructive Distillation of Coconut Shells, Coconut Husks, Coconut Rachises and Petioles and Rixe Hulls at 400°". *Univ. Philippines Natural and Applied Sci. Bull.*, 1935, **4**, 325–331.

ECONOMIC CONSIDERATIONS

Both Wells (1917) and Sudborough (1920) discuss the economic possibilities in their respective countries, the former giving a comprehensive list of questions which are important factors in plans for a wood distillation industry.

The chief difficulty in any country is the collection at a central factory of sufficient shells for distillation. It seems clear that any plan to undertake shell distillation would only be possible in cases where there is already some centralization of nuts for copra or desiccated coconut manufacture with the exception that it might be possible to modify charcoal manufacture so as to recover crude pyroligneous acid which might be collected for re-distillation at a central place. There are in Ceylon copra manufacturers and desiccated coconut mills capable of handling as many as 15 million nuts a year. This number of shells—some 2,300 tons or about 7 tons per working day—would suffice to keep running a fair-sized installation, using a still of about 30′ × 6′ diam. The shells in such factories are normally used for fuel directly, or burned to charcoal for use in gas engines.

Technically, as has been shown, coconut shells have definite advantages over most ordinary woods for distillation. A favourable feature in Ceylon is the existence of a considerable market for shell charcoal.

It is hoped that further information will accrue from semi-commercial trials projected by the Coconut Research Scheme. In the meantime, this article may be concluded by the writer's opinion that the development of any such industry as wood distillation would not be possible in Ceylon as an isolated project in normal times. It could only be considered in relation to other industrial development.

Interest only attaches to the subject at the present time in view of the possibility of it becoming necessary to meet war-time shortages or inflated prices of commodities essential to existing industries. It may be that no long-continued shortage of acetic acid or long period of high prices will occur, but it is obviously desirable to be prepared to meet such possible contingencies.

SUMMARY

(i.) Destructive distillation of coconut shells may be expected to give per 100 lb. shells, 34 lb. charcoal, 40 lb. pyroligneous acid (of up to 12·5 per cent. acetic acid content), 6 lb. of tar and 20 lb. of gas.

(ii.) 250 to 300 million coconut shells or about 40,000 tons are burned annually in Ceylon to produce about 13,600 tons of charcoal, without attempts to recover by-products. These would amount to about 16,000 tons of pyroligneous acid (equivalent to 2,000 tons acetic acid) and 2,400 tons of tar. The local rubber industry's requirements of acetic and formic acids do not exceed 500 tons annually.

(iii.) The production of finished chemical products such as glacial acetic acid (99 per cent.) and methyl alcohol cannot be contemplated in Ceylon. The most that could be contemplated is the production of a purified pyroligneous acid for rubber coagulation, and possibly of grey acetate for export. These are believed to be technically possible.

(iv.) The chief difficulties relate to collection and transport of raw material, and the centralization of charcoal production. The chief advantages are the existence of a market for charcoal and, if of sufficiently good quality, for acetic acid, and the fact that shells, by reason of their low moisture content and high acetic acid yield, are particularly suited for distillation.

(v.) The tar contains carbolic acid and creosote. It may be possible to make some use of this locally, but further experimental work is needed.

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