Synthesis of Vegetable-Based Activated Carbons with Mixed Micro- and Mesoporosity for Use in Cigarette Filters

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ABSTRACT: Activated carbons with micropores for adsorption and filtration of the volatile constituents of mainstream cigarette smoke, together with mesopores for enhanced mass transport were prepared by a novel route. Treatment of coconut shell or other lignocellulosic precursors with aqueous NaOH, followed by thorough washing, charring and steam activation produced carbons with enhanced adsorption characteristics in smoking trials, compared with their microporous analogues. The mechanism of formation of these carbons is explained in terms of initial partial dissolution of the precursor in an aqueous alkali solution, followed by catalytic gasification of carbon in steam involving residual sodium.

1. INTRODUCTION

Cigarette smoke is an aerosol stream containing an extremely complex and dynamic mixture of chemicals and approximately 5600 constituents have been identified to date (Perfetti and Rodgman 2011), many of which have been proposed as toxicants (Fowles and Dybing 2003; Cunningham *et al*. 2011). Tobacco smoke toxicants cover a range of chemical groups and functionalities (e.g. nitrosamines, polynuclear aromatic hydrocarbons and carbonyls), (Baker 1999; Green *et al*. 2007; Burns *et al*. 2008) as well as a range of volatilities, from permanent gases to compounds with very low vapour pressures at ambient temperatures.

Microporous activated carbons are well known as effective adsorbents in vapour phase filtration and as such would be expected to perform well as an additive in the cigarette filter for the removal of toxic vapours in cigarette smoke. A cigarette filter is typically composed of cellulose acetate fibres which are effective for the filtration of the smoke particulate phase (Norman 1999). On the other hand, vapour phase products of tobacco combustion are more readily adsorbed by activated carbon (Branton *et al*. 2011). However, the high flow rates involved when smoking (typically 1–1.5 dm^3/minute) and short contact times (of the order of milliseconds) can produce significant mass transport limitation to adsorption in the micropore system. Although the concentration of toxic species can be reduced using a microporous carbon filter, there is scope for improvement and modification of the porosity to incorporate mesopores is one way to achieve this (Branton *et al*. 2009). It has been reported (Branton and Bradley 2010; Bradley 2011) that if up to 50% of the total porosity is mesoporous, more effective adsorption of the toxic constituents of cigarette smoke occurs. Incorporation of mesopores is believed to facilitate increased diffusion

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to the micropores, enabling greater utilization of the whole micropore volume in the adsorption of vapour species.

Activated coconut shell carbon is incorporated in cigarette filters in some countries on a commercial scale, including Japan and Russia. It is an effective adsorbent, readily available and has the mechanical strength to withstand the high-speed production methods of cigarette manufacture. It is usually prepared from nutshell char by the steam or CO_2 physical activation method and is largely microporous. Direct chemical activation of nutshell with a chemical agent such as $ZnCl_2$, KOH or H_3PO_4 can also be used to create a wider porosity, depending on the ratio of precursor and chemical reagent (Derbyshire *et al*. 1995; Hu *et al*. 2001; Arjmand *et al*. 2006) At the end of the activation process, the chemical reagent, which can represent over 50% of the starting material mixture, is washed out of the activated carbon.

Carbons with tailored porosity can be manufactured via template methods (Lu *et al*. 2003; Fuertes and Alvarez 2004; Klepel *et al*. 2005) or from carbon aerogels (Horikawa *et al*. 2004; Perez-Caballero *et al*. 2008) but these processes can be complex, often require a well-defined precursor (e.g. a synthetic polymer) and can be expensive, especially when the final yield of activated carbon is calculated. This paper describes a simple method for the production of activated carbon having mixed micro- and mesoporosity and its performance in smoke filtration . The activated carbons are produced from coconut shells or other lignocellulosic precursors.

2. EXPERIMENTAL SETUP

2.1. Preparation

Comparison was made between carbons formed from coconut shell treated with different alkali solutions before the charring stage. Coarsely chopped (10–15 mm) coconut shell (100 g) was stirred at 50 °C for 4 hours in aqueous alkaline solution (300 cm^3, 1 M NaOH, 16 M NH_4OH or 1.5 M Na_2CO_3). All reagents were of general laboratory grade and were supplied by Fisher Scientific. The shell was then filtered and thoroughly washed with deionized water to minimize residual alkali content. After drying at 100 °C, the shell pieces were converted into a char by heating in a tube furnace (LTF 12/75/750, Lenton) to 600 °C for 4 hours under flowing N_2. When cool, the char was exposed to a flow of humid N_2 to deactivate the carbon surface and prevent exothermic adsorption of O_2 from the atmosphere which can cause over-heating or combustion. The charred shell was then crushed and sieved to give a particle size of 0.3–1.4 mm.

Samples (5 g) were then activated in a smaller tube furnace (LTF 12/25/250, Lenton) for 4 hours at 700 °C in steam, generated by water delivered at 5 cm^3/hour using a syringe pump and N_2 flow of 20 cm^3/minute. The products were designated as AC–NaOH, AC–NH_4OH and AC–Na_2CO_3. Final yields, based on the initial mass of char, were approximately 55%, 90% and 65%, respectively (Branton *et al*. 2010).

Control-activated samples used for comparison and designated AC-1 and AC-2 were prepared from water-washed shell and activated in steam to give approximately the same micropore volume as the AC–alkali samples. This was achieved at 85% yield (15% burnoff).

2.2. Characterization

Products were characterized by surface area measurement and residual sodium analysis. Surface areas were measured by nitrogen adsorption, after outgassing under vacuum for 4 hours at 350 °C, (ASAP 2020; Micromeritics). The Brunauer–Emmett–Teller (BET) equation, applied in the P/P_0

range 0.05–0.2, was used to calculate surface areas for all activated samples. Although not strictly applicable to adsorption in purely microporous solids (Gregg and Sing 1982), BET surface areas are routinely quoted in the characterization of activated carbons. Micropore volumes were calculated from the t plots and mesopore volumes from the desorption data according to the Barrett–Joyner–Halenda method. Sodium analysis was made by atomic absorption spectroscopy (AAnalyst 100 Flame, Perkin Elmer) on the filtered solutions from acid-digested samples.

2.3. Smoke Filtration Tests

A series of mixed porosity (micro + meso) activated carbons (AC–NaOH-1, AC–NaOH-2, etc.) was prepared by the above treatment process, together with their microporous analogue controls, having matched micropore volumes and prepared from water-washed coconut shell (AC-1 and AC-2).

   To assess the filtration properties of these carbons when incorporated in cigarette filters, the cigarette filters were prepared as follows: 60 ± 1 mg of the carbon granules were weighed into the cavity of a cigarette filter of a 24.6-mm circumference cigarette, made up of a 56-mm long tobacco rod containing a Virginia-style tobacco blend (tobacco rod density of 255 mg cm^{-3} at a moisture content of 13%) and a 27-mm length three-part cavity filter (10 mm cellulose acetate at the rod end, 4-mm cavity and 13 mm cellulose acetate at the mouth end). Triacetin is used as a plasticizer on cellulose acetate filter sections and loadings of 10% and 6% by weight for the mouth end and rod end segments, respectively, were used. Cigarette filters were all unventilated (i.e. no air vent holes are made to allow influx of air during puffing). A standard 50 CU permeability cigarette paper was used throughout [where 1 CU is the flow of air (cm^3/minute) passing through 1 cm^2 surface of the test piece at a measuring pressure of 1.00 kPa]. As a control, cigarettes of the same dimensions and composition were also prepared with an empty 4-mm filter cavity section. To mimic manufacturing conditions, the cigarettes were conditioned at 22 °C and 60% relative humidity for 3 weeks following the inclusion of carbon in the cigarette filter and then smoked under ISO smoking conditions (one 35-ml volume puff of 2-second duration taken every minute) (International Organisation for Standardisation 1991; Thomsen 1992). The smoke particulate phase was collected on a glass filter pad (known as a Cambridge filter pad) and subsequently analyzed to determine tar, water and nicotine yields. Smoke vapour phase was collected and analyzed using infrared for carbon monoxide, high-performance liquid chromatography for carbonyl compounds, continuous flow colorimetry for HCN and gas chromatography–mass spectroscopy for other volatile products detailed in the so-called Hoffmann list (Hoffmann and Hoffmann 1997), which is a list of chemical components in tobacco smoke. (Full details of all analytical methods used are described at www.bat-science.com.) Three replicates per smoke analyte were measured. Percentage reductions in smoke analytes relative to a cigarette containing no additive in the cavity were calculated. This serves as a useful technique for the screening of filter material activity in smoke.

3. RESULTS AND DISCUSSION

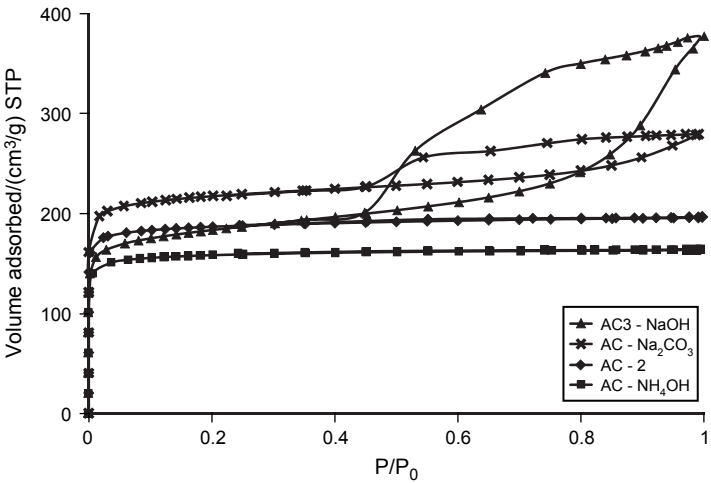### 3.1. Alkali-Treated Activated Carbons

Treatment of the coconut shell with the alkali solutions gave a red–brown liquor attributed to the partial dissolution of lignin, hemicellulose and other components, in a manner similar to the Kraft process, where the lignin is extracted from wood pulp by alkali in the paper making industry (Roberts 1996). The mass lost by the coconut shell following both NaOH and NH$_4$OH treatment

TABLE 1. Coconut Shell Mass Losses after Alkali Treatment

Coconut shell treatment	Mass (g)	Loss (%) based on	
		As received	Dried
As received	100	0	–
Dried	91	9	0
H$_2$O washed/dried	90	10	0
NaOH (M)/dried	84	16	8
Na$_2$CO$_3$ (1.5 M)/dried	91	9	0
NH$_4$OH (16 M)/dried	84	16	8

was 8%, based on the dry shell mass, (Table 1) and as such is considerably less than the typical lignin content (37%) of coconut shell (Woodruff 1979).

With the weaker alkali, Na$_2$CO$_3$, the solution during the soaking process remained paler than for the strong alkalis and the mass loss indicated that little, if any, material had been extracted from the coconut shell. Under identical activation conditions, only the activated carbons derived from NaOH-treated shell, and to a lesser extent, Na$_2$CO$_3$, were effectively activated and developed significant mesoporosity as shown by the nitrogen adsorption isotherm comparison in Figure 1 and the textural data in Table 2. The isotherms for carbons AC-2 and AC–NH$_4$OH, which were less reactive, are clearly type I, characteristic of microporous solids, whereas the remaining

Figure 1. Nitrogen adsorption isotherms for activated carbons prepared from alkali-treated coconut shell.

TABLE 2. Textural Properties of Activated Carbons Prepared from Alkali-Treated Coconut Shell

Activated carbon	Burnoff (%)	BET Surface Area (m^2 g^{-1})	Micropore Volume (cm^3 g^{-1})	Mesopore Volume (cm^3 g^{-1})
AC–Na$_2$CO$_3$	34	730	0.31	0.16
AC–NaOH	45	620	0.22	0.49
AC–NH$_4$OH	11	530	0.25	0.01
AC-2	15	620	0.29	0.03

Abbreviation: BET, Brunauer–Emmett–Teller.

adsorption isotherms show increasing adsorption at higher pressures and hysteresis, characteristic of adsorption in mesopores (Gregg and Sing 1982).

Despite the extended washing to remove the excess alkali, it was found on analysis that a low residue (1 %) of Na existed in the shell treated with NaOH and Na_2CO_3 solutions. This is a much lower concentration than that usually needed for pure chemical activation but was impossible to remove completely by washing before the heat-treatment stages and was found to be concentrated by the charring and activation processes (Table 3). Final washing after activation was shown to remove the majority of the remaining Na, presumably because the pore system made it accessible.

Because little mesoporosity was formed in the activated carbon after Na_2CO_3 treatment of the shell (no dissolution) and none after NH_4OH treatment (dissolution, but absence of Na) these observations indicate that for significant mesopore development at 700 °C, both the partial dissolution process and the presence of residual Na are important. Furthermore, it was shown that merely heating the char

TABLE 3. Sodium Analysis Based on Dry Weight for Each of the Sample Stages in the Preparation of Activated Carbon from NaOH-Treated Coconut Shell

Sample	% Na
Coconut shell	0.03
Washed NaOH-treated shell	1.34
Char	3.06
Activated carbon	7.96
Washed activated carbon	0.56

prepared from NaOH-treated and washed shell in nitrogen alone at 700 °C produced no significant porosity and the sample had a surface area of only 0.65 m^2 g^{-1} (as measured by krypton adsorption). This indicates that a steam atmosphere is also required for the activation process to produce mesoporosity. The preparation method, therefore, differs from conventional chemical activation of a carbon precursor as only trace amounts of species from the chemical activation agent (Na) are present and an oxidizing atmosphere (steam) is required. Because it is well known that alkali metals are catalysts for carbon gasification (McKee 1983; Matsumoto and Walker 1986), it is probable that the residual sodium, present at very low concentration as the hydroxide or carbonate, has a catalytic effect on the carbon gasification in the regions where lignocellulosic material has been dissolved, causing the development of mesopores. Although the scope of this study was not extended to include alkali-treated precursors with higher residual amounts of Na, it is likely that this would tend to increase the development of mesoporosity via a purely chemical activation route, at the expense of the micropore development, which could ultimately decrease the adsorption capacity. A separate investigation of the effect of a range of residual Na concentrations on the activation process and filter performance will be completed and published separately. The NaOH treatment method is applicable to the pore development of a wide range of lignocellulosic materials as demonstrated by the surface area and

TABLE 4. Textural Properties of Activated Carbons Prepared from NaOH-Treated Lignocellulosic Precursors

Carbon precursor	Burnoff (%)	BET surface area (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Mesopore volume (cm^3 g^{-1})
Pistachio shells	44	720	0.28	0.35
Oak chips	38	560	0.20	0.38
Bamboo	52	530	0.14	0.50
Almond shells	43	550	0.18	0.51

TABLE 5. Reductions in the Level of Smoke Constituents using Microporous and Mesoporous Carbon Filters

	Carbon							
	None	AC-1	AC–NaOH-1	AC–NaOH-2	None	AC-2	AC–NaOH-3	AC–NaOH-4
Micropore vol/cm^3 g^{-1}	–	0.18	0.17	0.17	–	0.29	0.34	0.23
Mesopore vol/cm^3 g^{-1}	–	0.04	0.37	0.38	–	0.03	0.49	0.45
Smoke yield (% reduction)								
Puff no. (per cig)	6.9	7.0	7.3	6.9	6.8	6.5	6.5	6.7
NFDPM (mg/cig)	11.9	11.1	10.9	10.4	10.8	10.6	9.1	9.8
Nicotine (mg/cig)	0.92	0.94	0.91	0.88	0.85	0.86	0.72	0.76
Water (mg/cig)	1.8	1.7	1.7	1.5	1.8	1.7	1.2	1.3
CO (mg/cig)	10.6	10.4	10.5	10.4	9.2	9.8	8.9	9.3
Acetaldehyde (µg/cig)	527	520 (1)	399 (24)	418 (21)	468	447 (5)	320 (32)	379 (19)
Acetone (µg/cig)	270	261 (3)	177 (34)	174 (35)	242	230 (5)	112 (54)	162 (33)
Acrolein (µg/cig)	60.0	60.3 (0)	36.3 (40)	38.1 (37)	52.5	45.8 (13)	20.2 (62)	32.2 (39)
Butyraldehyde (µg/cig)	35.5	34.9 (2)	19.0 (46)	18.7 (47)	32.9	30.8 (6)	12.1 (63)	17.6 (47)
Crotonaldehyde (µg/cig)	20.5	20.7 (–1)	10.3 (50)	10.0 (51)	17.9	16.4 (8)	5.6 (69)	9.6 (46)
Formaldehyde (µg/cig)	38.6	37.5 (3)	21.5 (44)	23.0 (40)	30.9	27.2 (12)	18.9 (39)	20.8 (33)
Methyl ethyl ketone (µg/cig)	65.0	61.4 (6)	37.5 (42)	35.3 (46)	61.3	57.5 (6)	22.1 (64)	34.7 (43)
Propionaldehyde (µg/cig)	44.0	42.7 (3)	28.2 (36)	27.8 (37)	41.8	38.8 (7)	19.2 (54)	26.3 (37)
HCN (µg/cig)	135	113 (16)	90.7 (33)	68.8 (49)	123	111 (10)	62.1 (50)	74.5 (40)
1,3-Butadiene (µg/cig)	38.4	37.8 (2)	34.5 (10)	30.7 (20)	63.5	58.2 (8)	42.9 (32)	44.8 (29)
Acrylonitrile (µg/cig)	12.7	11.8 (7)	9.3 (27)	8.0 (37)	17.0	13.3 (22)	7.1 (58)	8.2 (52)
Benzene (µg/cig)	49.3	47.1 (4)	32.9 (33)	27.3 (45)	53.3	46.1 (14)	20.9 (61)	24.6 (54)
Isoprene (µg/cig)	506	506 (0)	407 (20)	351 (31)	593	544 (8)	296 (50)	327 (45)
Toluene (µg/cig)	73.9	70.0 (5)	40.7 (45)	32.6 (56)	74.7	60.8 (19)	23.4 (69)	27.9 (63)
Average reduction (%)	–	4	35	40	–	10	54	41

Abbreviation: NFDPM, Nicotine-free dry particulate matter.

porosity data in Table 4. These materials have not been investigated in smoke filtration, but could potentially be alternative adsorbents for this purpose.

Future studies of the range of activated carbons prepared by this general method applied to different precursors will also include scanning electron microscopic images to show their different morphologies. Filtration performance may then be correlated with porosity, as demonstrated, precursor Na concentration and morphology of precursor/activated carbon.

3.2. Smoke Tests

Table 5 lists the concentration and percentage reduction of volatile constituents in the mainstream smoke under the ISO machine-smoking condition, achieved using carbon in the filter, compared with the scientific control without the carbon. The micropore volumes of the carbons reported in Tables 2 and 4 are relatively low for an activated carbon, but samples were selected to highlight the effect of the introduction of mesopores on the adsorption of the volatile smoke constituents. In such cases it has been proposed that the accessible micropore volume is quickly saturated (Branton *et al*. 2009), so effect of improved diffusion via introduced mesoporosity is readily observed. It is generally accepted that in a cigarette filter, filtration of these volatile species occurs in the carbon micropores (Mola *et al*. 2008) and is therefore proportional to the micropore volume in a purely microporous sample. The high adsorption potential within the micropores is responsible for the largely non-discriminatory retention of both polar and non-polar species in the table. In the present study, the low micropore volumes of control samples AC-1 and AC-2 have no affect on the smoke filtration (differences of less than 10% are generally not significant).

However, when mesopores are also present [AC–NaOH-(1–4)], the percentage reductions in the smoke-volatile compounds rise significantly. This is thought to be due to the ability of the mesopores to act as transport pores (Branton *et al*. 2009) and thus increase the utilization of the micropore filtration properties in the activated carbon. AC–NaOH-1 and 2 with similar micropore and mesopore volumes give very similar smoke filtration performance. AC–NaOH-3 gives greater reductions than four in the smoke vapours measured due to an increased volume of micropores in the carbon.

4. CONCLUSIONS

Steam activation of a range of chars derived from lignocellulosic precursors has been shown to produce activated carbons with significant mesoporosity, provided the precursors are treated with aqueous NaOH solution, followed by thorough washing to remove as much of the residual alkali as possible. It is thought that mesopore development depends on three factors: (i) partial dissolution of some of the lignocellulose components, (ii) catalysis of carbon gasification by residual Na and (iii) the provision of an oxidizing atmosphere for the activation. The activated carbons thus prepared were found to enhance the capability to decrease the concentration of the volatile components in cigarette smoke when compared to carbons with the same degree of microporosity, but no mesopores. This can be explained by the effect of better mass transport provided by the mesopores, enabling greater access to the micropores where the organic vapour molecules are actually adsorbed in a fast-flow smoke stream.

REFERENCES

Arjmand, C., Kaghazchi, T., Latifi, S.M. and Soleimani, M. (2006) *Chem. Eng. Technol.* **29,** 986.

Baker, R.R. (1999) Smoke Chemistry. In: Davis, D.L. and Neilson, M.T. Eds, *Tobacco: Production, Chemistry and Technology*. Blackwell Science, Oxford.

Bradley, R.H. (2011) *Adsorpt. Sci. Technol.* **29,** 1.

Branton, P. and Bradley, R.H. (2010) *Adsorpt. Sci. Technol.* **28,** 3.

Branton, P., Lu, A.H. and Schuth, F. (2009) *Carbon* **47,** 1005.

Branton, P.J., Dawson, E.A. and Parkes, G.M.B. (2010) Method of preparing porous carbon. GB Patent Application 1007667.7.

Branton, P.J., McAdam, K.G., Duke, M.G., Mola, M., Curle, M., Procter, C.J. and Bradley, R.H. (2011) *Adsorpt. Sci. Technol.* **29,** 117.

Burns, D.M., Dybing, E., Grey, N., Hecht, S., Anderson, C., Sanner, T., O'Conner, R., Djordjevic, M., Dresler, C., Hainaut, P., Jarvis, M., Opperhuizen, A. and Straif, K. (2008) *Tob. Control* **17,** 132.

Cunningham, F.H., Fiebelkorn, S., Johnson, M. and Meredith, C. (2011) *Food Chem. Toxicol.* **49,** 2921.

Derbyshire, F., Jagtoyen, M. and Thwaites, M. (1995) Activated carbons—production and applications. In: Patrick, J.W. Ed. *Porosity in Carbons: Characterisation and Applications*. Edward Arnold, London.

Fowles, J. and Dybing, E. (2003) *Tob. Control* **12,** 424.

Fuertes, A.B. and Alvarez, S. (2004) *Carbon* **42,** 3049.

Green, C.R., Schumaker, J.N., Lloyd Jr, R.A. and Rodgman, A. (2007) *Beitr. Tabakforsch*. **22**.

Gregg, S.J. and Sing, K.S.W. (1982) *Adsorption Surface Area and Porosity,* Academic Press, London.

Hoffmann, D. and Hoffmann, I. (1997) *J. Toxicol. Env. Health* **50,** 307.

Horikawa, T., Hayashi, J. and Muroyama, K. (2004) *Carbon* **42,** 1625.

Hu, Z.H., Srinivasan, M.P. and Ni, Y.M. (2001) *Carbon* **39,** 877.

International Organisation for Standardisation (1991) ISO 3308: Routine analytical cigarette smoking machine—definitions and standard conditions.

Klepel, O., Garsuch, A. and Bohme, K. (2005) Comparative studies of the templated synthesis of porous carbon materials. In: Cejka, J., Zilkova, N. and Nachtigall, P. Eds, *Molecular Sieves: From Basic Research to Industrial Applications, Pts A and B*. Elsevier, Amsterdam.

Lu, A.H., Schmidt, W., Spliethoff, B. and Schuth, F. (2003) *Adv. Mater.* **15,** 1602.

Matsumoto, S. and Walker, P.L. (1986) *Carbon* **24,** 277.

McKee, D.W. (1983) *Fuel* **62,** 170.

Mola, M., Hallum, M. and Branton, P. (2008) *Adsorption* **14,** 335.

Norman, A. (1999) Smoke Chemistry. In: Davis, D.L. and Neilson, M.T. Eds, *Tobacco: Production, Chemistry and Technology*. Blackwell Science, Oxford.

Perez-Caballero, F., Peikolainen, A.L., Uibu, M., Kuusik, R., Volobujeva, O. and Koel, M. (2008) *Microporous Mesoporous Mat*. **108,** 230.

Perfetti, T.A. and Rodgman, A. (2011) *Beitr. Tabakforsch*. **24,** 215.

Roberts, J.C. (1996) *The Chemistry of Paper*. Royal Society of Chemistry, London.

Thomsen, H.V. (1992) *Recent Adv. Tob. Sci*. **18,** 69.

Woodruff, J.G. (1979) *Coconuts: Production, Processing, Products*. AVI Publishing Co. Inc, New York.