Effect of nitric acid digestion on organic materials and silica in rice husk

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Studies on the digestion of rice husk by HNO_3 at 65 °C over 2–12 h have been carried out. Changes in the physical characteristics and morphology of rice husk due to the degradative effect of nitric acid were studied by using thermogravimetric analysis and scanning electron microscopy. It was observed that the residue obtained after 12 h digestion is a mixture of loose cellulose fibres and fragments of a cellulose–silica composite consisting mainly of cellulose (*ca.* 24%) and silica (*ca.* 76%), respectively.

Rice husk, a thin but abrasive skin in nature, covering the edible rice kernel is abundant in Malaysia. It has been reported[1] that Malaysia produces *ca.* 18 million tonnes of paddy in which about one fifth of it is the husk. This means that there is a steady supply of *ca.* 3.6 million tonnes of rice husk annually.

The constituents of rice husk are, cellulose, 32.7%, hemicellulose, 20.5%, lignin, 21.8%, silica, 15.1%, solubles, 2.8% and moisture, 7.5%.[2] A high silica content ash can be obtained through combustion of the husk in air at a temperature as low as 600 °C.[3,4]

Both rice husk and rice husk ash are potential raw materials for ceramics, cements and silica-based industries. However, most of the rice producing countries are developing countries and lack advanced technology to convert rice husk into valuable materials.

The production of Si_3N_4, sialon and SiC are well documented in the literature.[8–11] The production of these materials can be done on a large scale and is expected to be energy and cost saving in comparison with the normal raw materials, sand and coal.

Rice husk silica has been used in the preparation of many types of zeolite.[12,13] A number of studies on converting rice husk into activated carbon have also been reported.[14–16] In all cases, rice husk was pyrolysed in an inert atmosphere in order to remove volatile organic materials leaving behind highly porous carbonaceous materials.

The present paper reports a part of a series of work on rice husk.[2,3,8–10,17] The paper's emphasis is on a systematic digestion of rice husk by nitric acid in order to produce porous materials which can be used as adsorbents. A comparative study of the products is also highlighted.

Experimental

Rice husk was obtained from a Rice Mill at Yan, Kedah, Malaysia. The husk was first washed with distilled water to remove any adhering materials and dried. The husk (10 g) was digested with 100 ml of concentrated of nitric acid at 65 °C on a hot plate for 2–12 h. The digested husk was then washed with distilled water until the washing was neutral, oven dried at 110 °C for 1 h, and ball milled to pass a 75 μm sieve. The samples were labelled as RRH, TRH2, TRH4, TRH8 and TRH12. RRH denotes raw rice husk and TRH2 denotes residue obtained after 2 h digestion, and so forth. TRH12 was further treated by using the TAPPI procedure[7] to isolate cellulose and labelled as S12. Commercial cellulose (Sigma Chemical Co.) was used as a reference.

The milled sample was continuously extracted with 200 ml of a boiling ethanol–benzene solvent mixture for 6 h in a Soxhlet extractor based on the TAPPI procedure.[5] The extracted sample was dried in an oven at 110 °C for 1 h. Organic constituents of the husk and digested husk were analysed by procedures adapted from Wise *et al.*[6] and that of the TAPPI procedure.[7] The sample was also analysed by thermogravimetry using a Perkin-Elmer TGA-7 Series model. All samples were heated in flowing oxygen at a rate of 20 °C min^{-1} from 40 to 900 °C. The purpose is to study the changes in thermal behaviour of the various residues and use these results to interpret the changes in composition and morphology as a result of degradative nitric acid digestion and the effect of varying duration of treatment. Scanning electron microscopy (SEM) using a Cambridge S360 model was also used to study the changes in the structure and morphology of the residues. The sample was glued to an aluminium stub and coated with a thin layer of gold.

Results and Discussion

Acid digestion

The compositions of raw rice husk and digested husks are listed in Table 1. The organic materials were comprised of cellulose, hemicellulose and lignin. It is observed that hemicellulose and lignin are readily digested by HNO_3 as is evident from the significant overall loss in mass after even 2 h of treatment. The reaction was vigorous and exothermic.[9] After 10 h of digestion, the amounts of hemicellulose and lignin are *ca.* 0.8 and 0.5%, respectively. Further loss of lignin was observed after 12 h digestion. Interestingly, however, cellulose behaves differently when compared to hemicellulose and lignin. It is observed that *ca.* 6% cellulose remained even after 12 h digestion. This result indicates a high degree of resistance of the residual cellulose in the husk towards acid digestion.

Overall, it is evident that hemicellulose and lignin are readily digested into simple species while cellulose is only partially digested. The difficulty of digesting cellulose may be related to its partially crystalline nature.[17] The silica content is found to be in the range 16–22%, in agreement with results reported elsewhere.[3,18]

Table 2 gives the compositions of the digested residues. The physical appearance of the residue differs from that of the raw husk. The particle size of the husk decreases with increase in the digestion time. After 10 h digestion, for example, the rice husk has been reduced to a powdery form that can readily pass through a 75 μm sieve. The change in colour during digestion is also remarkable. The original dark brown colour of the rice husk changed to yellowish and light yellow on increasing the time of digestion. After 12 h digestion, the residue was white since negligible amounts of lignin were present in the sample. At this stage the sample consists of a finely degraded cellulose–silica skeleton which contains *ca.* 26% cellulose and *ca.* 74% silica and negligible amounts of lignin.

Table 1 Composition as percentage of organic mass of raw rice husk and residues based on raw rice husk

	sample						
	RRH	TRH2	TRH4	TRH6	TRH8	TRH10	TRH12
cellulose	35.5	8.5	7.7	7.0	7.0	6.4	5.9
hemicellulose	22.3	4.0	2.3	1.7	1.1	0.8	0.8
lignin	13.6	3.0	1.9	1.3	0.7	0.5	trace
silica	16.1	20.3	20.2	20.7	21.6	20.7	19.2
solubles	3.3	0.1	0.1	trace	trace	trace	trace
moisture	9.1	—	—	—	—	—	—
loss	—	65.0	68.0	70.0	70.0	72.0	74.0
total	99.9	100.9	100.2	100.7	100.4	100.4	99.9

Table 2 Composition as percentage of organic mass in the residues obtained from digestion of rice husk with concentrated nitric acid at 60 °C as compared to the raw husk

	sample						
	RRH	TRH2	TRH4	TRH6	TRH8	TRH10	TRH12
silica	16.1	58.0	63.0	69.0	72.0	74.0	74.0
cellulose	35.5	24.4	24.0	23.2	23.2	23.0	22.8
hemicellulose	22.3	11.4	7.1	5.2	3.5	3.0	3.1
lignin	13.6	8.6	6.1	4.2	2.4	1.9	0.2
solubles and moisture	12.5	—	—	—	—	—	—

The action of nitric acid on rice husk can be understood by considering the reactivity of the individual constituents of rice husk. Cellulose, $(C_6H_{10}O_5)_n$, is a homopolysaccaride of the β-glucose unit which is connected by the glycosidic linkage to C-4 of neighbouring units to form strong structures such as in rice husk. The cellulose is crystalline and the degree of crystallinity varies considerably depending on the origin of the sample. For rice husk, data on the crystallinity of cellulose is not available to date. However, evidence of its occurrence has been reported earlier.[17] The report further showed a significant loss in cellulose after nitric acid treatment and attributed it to the degradation of the amorphous region of the cellulose fibres in rice husk. The strong oxidising effect of nitric acid and the amorphous nature of the cellulose fibres are the contributing factors to the loss of cellulose. Indeed, the combined effect of the above two factors is also seen as being responsible for the significant loss of cellulose after first 2 h digestion as shown in Tables 1 and 2. Longer digestion times result in only a gradual decrease and after 12 h, *ca.* 6% (in the raw husk) and *ca.* 23% (in the residue) of cellulose still remained. This suggests its resistivity and what remains may be associated with the crystalline fraction of degraded cellulose and the undegraded fraction that is still embedded in the silica matrix. This is revealed by scanning electron microscopy as discussed later.

Hemicelluloses are heteropolysaccarides comprised mainly of glucose, mannose, galactose, xylose and arabinose residues randomly distributed in the main chain. They are readily attacked in nitric acid to form soluble species. However, a very small percentage still remains after 12 h digestion. This could be due to the fraction which is still embedded within the silica matrix in the rice husk. A similar rate of loss was also observed in lignin which was easily attacked by nitric acid. During acid digestion, a brown gas, presumed to be nitrogen oxides, was evolved at the early stage of reactions.

Thermogravimetric analysis

Thermogrametric analyses of raw rice husk and the residues obtained from nitric acid digestion are shown in Fig. 1–4. The results provide further evidence of degradation of the lignocellulosic material present in raw rice husk. The initial temperatures of thermal degradation and the rates of mass loss obtained from the thermogravimetry and differential thermog-

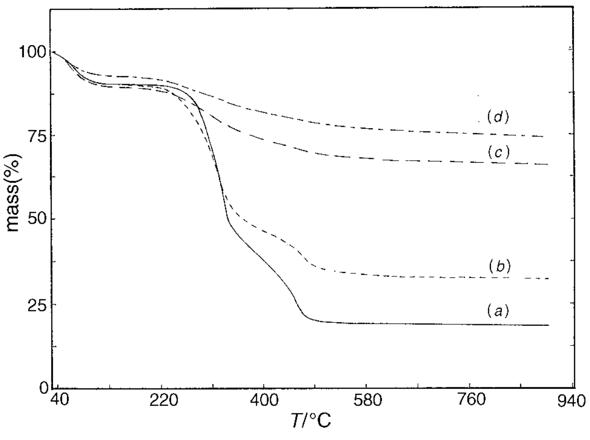

Fig. 1 Thermogravimetry curves of (*a*) RRH, (*b*) TRH4, (*c*) TRH8 and (*d*) TRH12

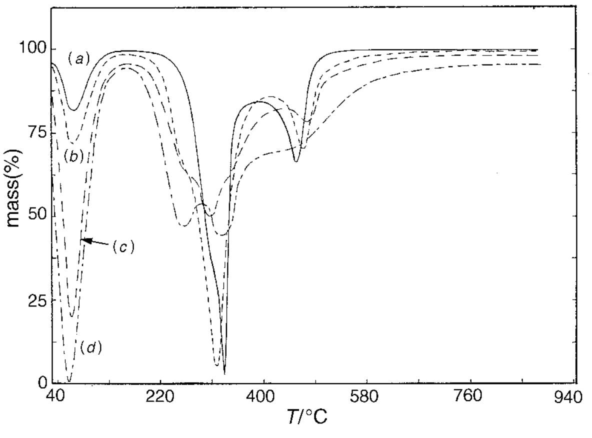

Fig. 2 Differential thermogravimetry curves of (*a*) RRH, (*b*) TRH4, (*c*) TRH8 and (*d*) TRH12

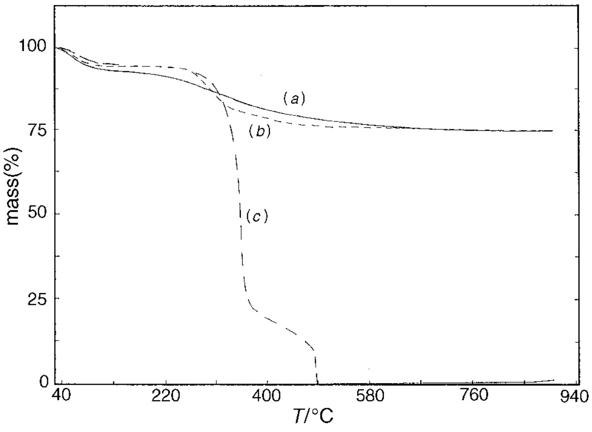

Fig. 3 Thermogravimetry curves of (*a*) TRH12, (*b*) S12 and (*c*) reference cellulose

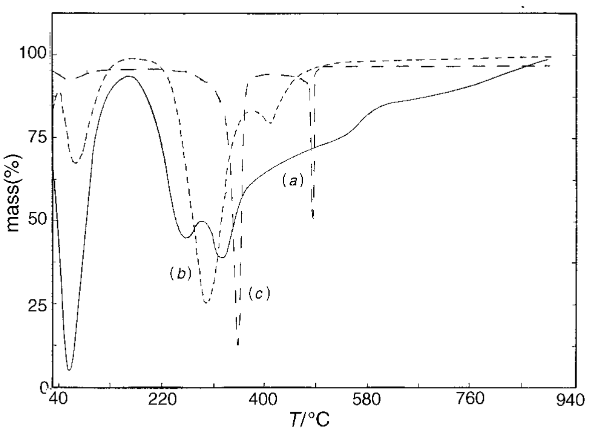

Fig. 4 Differential thermogravimetry curves of (*a*) TRH12, (*b*) S12 and (*c*) reference cellulose

ravimetry curves have enabled us to understand some of the physical characteristics and changes in rice husk and residues as a result of nitric acid digestion.

Fig. 1(*a*) shows the characteristic thermoxidative decomposition of raw rice husk up to 900 °C. This is a three-stage mass loss with an initial mass loss below *ca.* 100 °C, owing to evaporation of adsorbed water. The second stage of mass loss, *i.e.* between 230 and 370 °C, represents the thermal degradation of organic components comprising mainly cellulose, hemicelluloses and lignin. Here the formation and vaporisation of volatile products is believed to be the dominant process. The third stage represents another mass loss but at a much slower rate. The pattern observed is similar to that of the reference cellulose [Fig. 3(*c*)]. According to Yang and Kotot,[21] the third stage of mass loss in the thermogravimetry curve of the cellulose that they studied was due to oxidation of the charred residue formed during pyrolysis. The lignocellulose content of rice husk is presumably pyrolysed to char under the thermal conditions used in this study. Thus the third stage of mass loss observed in the present thermogravimetry curve of rice husk is attributed to oxidation of the charred residue formed during pyrolysis of the rice husk. The remaining mass of *ca.* 17% represents the silica content of the raw rice husk which is comparable to the value obtained from the chemical analysis as given in Table 1.

Comparison of the thermogravimetry curve of rice husk [Fig. 1(*a*)] to that of the reference cellulose [Fig. 3(*c*)] also shows that the initial temperature of thermal degradation in rice husk is lower (*ca.* 230 °C) than that of the cellulose (*ca.* 270 °C). This may be attributed to the presence of hemicellulose and lignin in rice husk which influences the initial temperature of degradation. Crystallinity, molecular mass, and impurities are known to influence the initial temperature of the thermal degradation of cellulose.[21] In rice husk, the amorphous and low molecular mass hemicellulose and lignin are expected to degrade earlier and faster relative to cellulose which is assumed to have higher molecular mass and a certain degree of crystallinity. Interestingly, this relative difference in the initial degradation temperature is evident in the differential thermogravimetry curve of raw rice husk [Fig. 2(*a*)] which exhibits a broad peak with a noticeable shoulder, corresponding to two phases of degradation in the temperature range 230–370 °C whereas only a single peak is seen in the reference cellulose [Fig. 4(*c*)]. The shoulder, appearing at lower temperature than that of the peak, is likely to be associated with the degradation of the lignin–hemicellulose components. The peak is believed to be associated with cellulose because its maximum rate of the mass loss peak occurs at *ca.* 330 °C which is comparable to that of the reference cellulose, *ca.* 350 °C.

The thermogravimetry curve of the residue obtained after 4 h digestion exhibits a behaviour similar to that of the rice husk except for the apparent change to a lower initial temperature of degradation, *ca.* 180 °C. We suggest that nitric acid digestion has broken down the rice husk into small fragments thus exposing more organic materials at or just beneath their surfaces and has also let loose some of the cellulose fibres initially embedded in the rice husk structure. Such exposed organic constituents in the residues are expected to be more readily pyrolysed than those still embedded in the rice husk structure and may explain the lower thermal degradation temperature observed here. As for the higher silica content observed, *ca.* 38%, it indicates the overall decrease in the insoluble fractions of the organic matters in the residue. The differential thermogravimetry curve of the sample [Fig. 2(*b*)] still exhibits the presence of the two phases of degradation as in rice husk although the initial temperature seems to be slightly shifted to a lower value.

The effect of 8 and 12 h of digestion is reflected in an even greater loss of the lignocellulose components as evident from the increasing final mass of *ca.* 69 and 75%, respectively, representing residual silica. This is shown in Fig. 1(*c*) and (*d*). This observation suggests that even after 12 h digestion the lignocellulosic material is still present implying strong resistance to nitric acid digestion. One reason may be the structural morphology of the rice husk composite which possesses high resistance to nitric acid penetration and attack so that even the small fragments which are formed after digestion are still intact. In other words, these fragments contain hemicelluloses and cellulose still embedded in the silica matrix as they were in rice husk. Another reason could be that there are loose cellulose fractions that still remain in the residues which could be crystalline fibres. The scanning electron micrograph in Fig. 5(*c*) reveals the physical nature of fragments in the residues.

The differential thermogravimetry curves after 8 and 12 h treatment shown in Fig. 2(*c*) and (*d*), respectively, appear to provide clearer evidence that may strengthen the above perception about the general structure and morphology of the residues. Firstly, it is apparent that the rate of mass loss of both residues is much slower than that of the rice husk (and the residue obtained from the 4 h digestion) as evident from a much broader peak in both cases. Such a slow rate of degradation can only be explained by the absence of exposed organic materials. Certainly there are loose crystalline fibres of cellulose present but this is not sufficient to affect the overall rate of mass loss. Thus, the fragmented form of the residue and the morphology of the individual particle, as seen earlier, seems to provide an explanation of the above observation. Secondly, the phases of degradation differentiating between hemicelluloses and cellulose are more apparent. This is reflected by

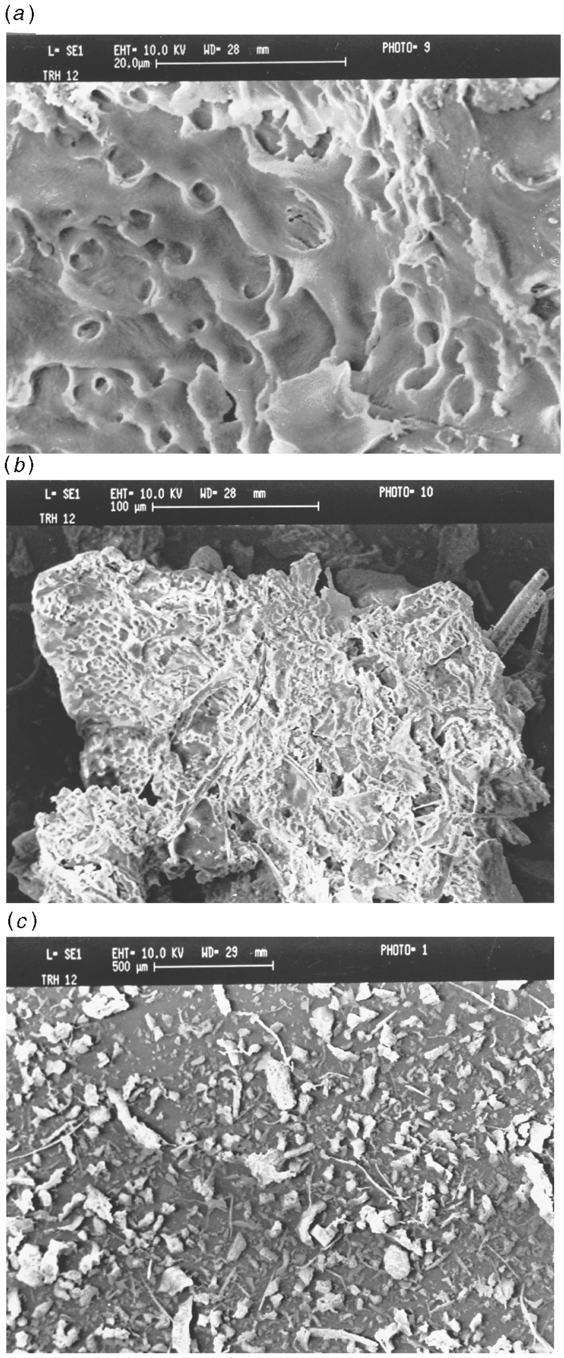

Fig. 5 Scanning electron micrographs of TRH12 [bars: (*a*) 20 μm, (*b*) 100 μm, (*c*) 500 μm]

the appearance of two distinct peaks in the same temperature range, *i.e.* 220–370 °C and the two peaks appear to be completely separated in the 12 h sample. The above evidence suggests that both hemicelluloses and cellulose are present in the residues but intact in the fragments. The actual morphology of the fragments is shown in the scanning electron micrograph in Fig. 5(*b*) and compares well with the above descriptions. However the actual nature of their coexistence in the silica matrix is still unclear.

To prove that the two peaks observed in differential thermogravimetry curve of the TRH12 sample correspond to those of the hemicelluloses and cellulose degradation respectively, we tried to separate the two components using the TAPPI procedure.[7] This treatment should finally produce a residue comprising only cellulose and silica, denoted as S12. The residue was subsequently characterised using thermogravimetry as described earlier. The thermogravimetry and differential thermogravimetry curves are shown in Fig. 3(*b*) and Fig. 4(*b*), respectively. Significant changes are observed after the treatment, especially in the differential thermogravimetry curve where a complete disappearance of the peak presumably associated with the hemicellulose degradation is observed. This confirms the presence of hemicelluloses in the TRH12 residues. It also suggests that the TAPPI treatment on the TRH12 residues removes all the degraded and insoluble organic species, except for the crystalline cellulose, formed during digestion. The peak associated with the cellulose degradation is apparently enhanced suggesting a greater rate of mass loss. Such changes suggest that the cellulose fraction in the S12 sample may have been disembedded from the silica matrix, *i.e.* in loose fibrous form, and its thermal degradation is therefore more easy compared to the embedded state. However, the rate of mass loss is still lower than that of the reference cellulose [Fig. 4(*c*)]. This is an indication that the cellulose in S12 is fairly crystalline in nature. Another interesting feature is the onset temperature, *ca.* 200 °C, which is lower than that of the reference cellulose (*ca.* 265 °C). This is unexpected if we assume the reference cellulose to be less crystalline than the cellulose in S12, which is believed to be very highly crystalline, because the latter is expected to degrade at higher temperature than the former, as suggested elsewhere.[19–21] We are inclined to attribute this to the effect of impurities as suggested by Basch *et al.*[22] Although a systematic analysis of the impurity content in all the samples studied was not performed, we believe that impurities are present, because of exposure to HNO_3 during treatments. In fact, the decreasing trend of the onset temperatures with increase in digestion time, as shown in Fig. 2, seems to point to such an effect.

Scanning electron micrographs

The scanning electron micrographs of rice husk and residues obtained after different times of treatment reveal a general breakdown of the rice husk structure to small fragments of irregular shapes. The size of these fragments was observed to decrease as the duration of digestion increased. The presence of fibrous species among the fragment particles in the residues is likely to be cellulose, probably degraded and highly crystalline in nature.

Fig. 5 shows scanning electron micrographs of the TRH12 residue. The general physical appearance, as described above, is evident in Fig. 5(*c*). A closer view of an individual particle reveals a porous composite comprised of a significant amount of fibrous structures embedded within a dense matrix [Fig. 5(*a*) and (*b*)]. Based on the data in Table 2 which indicates the presence of 74.0% silica, 22.8% cellulose, 3.1% hemicellulose and 0.2% lignin in this residue and the mass% obtained from the thermogravimetry curve for TRH12, it can be inferred that the particle is a composite comprising cellulose fibres, hemicellulose and lignin embedded within a dense matrix of silica. The numerous holes observed could be the original sites of the cellulose fibres, now existing as loose fibres, which have been removed during acid digestion.

The above physical structures of the residues and morphologies of the particles may be taken as representative of the changes as a result of nitric acid digestion on the rice husk. Apart from the effect on the extent of degradation of the lignocellulose materials, increasing time of digestion has also been shown to disintegrate rice husk to smaller particles.

Fig. 6 compares the morphology of ash obtained from the TRH12, S12 and reference cellulose samples. The ash exhibits a skeletal structure believed to be silica, practically free of organic material [Fig. 6(*a*)]. Another interesting observation

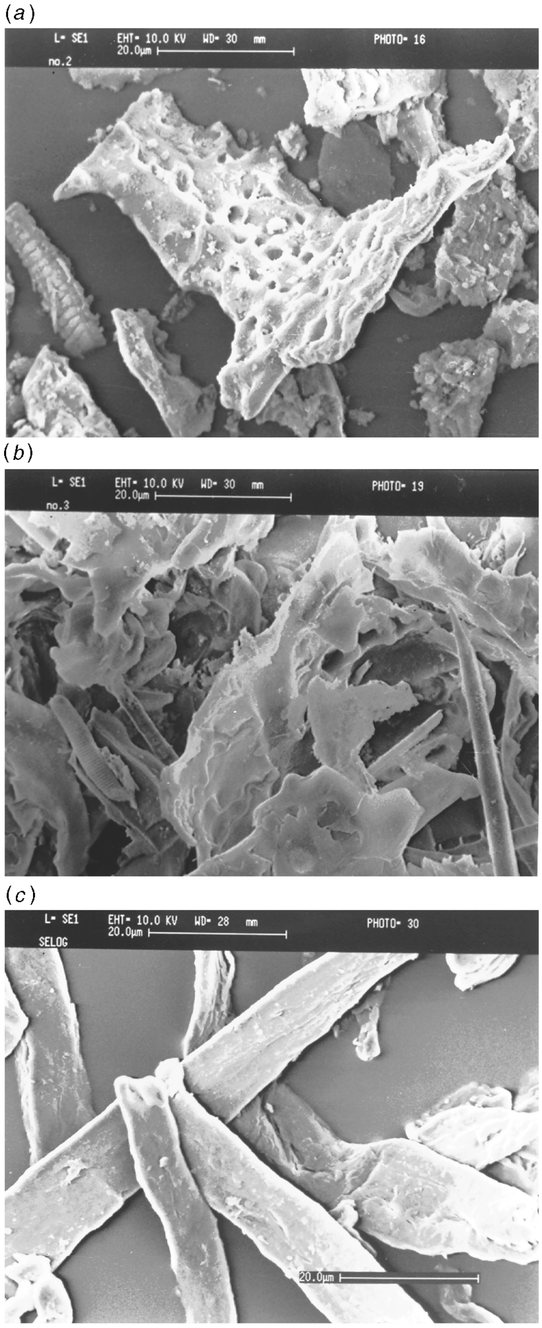

Fig. 6 Scanning electron micrographs of (*a*) ash obtained from TRH12, (*b*) S12 and (*c*) reference cellulose (bars = 20 µm)

made from scanning electron micrographs is the effect of TAPPI treatment carried out on the TRH12 residue. Fig. 6(*b*) shows the micrograph of S12 where the dense characteristic of the silica matrix, as in TRH12, has been destroyed. It seems that the cellulose fibres have been disembedded. This is to be expected as the TAPPI treatment is intended to degrade lignin and hemicelluloses sequentially to soluble species. Therefore what is left is only cellulose and silica. This is also confirmed by the thermogravimetric analysis of sample S12 where it was observed that the peak associated with hemicellulose was absent while the rate of mass loss associated with cellulose was enhanced. Such enhancement is attributed to the more efficient thermal initiation and depolymerisation of cellulose in the loose fibrous state in S12 compared to the embedded state in TRH12.

Fig. 6(*c*) shows a micrograph of the reference cellulose. The difference in terms of the fibre length and diameter of cellulose between that of the rice husk and the reference cellulose is clear. This serves as one of the reasons for the differences in their thermal behaviour observed in this study, *i.e.* the composite nature of the rice husk.

Conclusion

Chemical analysis data shows that cellulose, hemicellulose and lignin have been digested by HNO_3. The general physical change following digestion is the disintegration of the rice husk structure to small fragments comprising particulates and fibrous structures. The particles are irregular in size which decreases as digestion time increases. The thermogravimetric analysis of the residues suggests that the hemicellulose, lignin and cellulose that are still present after digestion are embedded within the dense silica matrix except for few loose cellulose fibres. The individual particles are in fact porous composites believed only to be partially in its natural form. The data from thermogravimetric and scanning electron microscopy analyses appear to be in agreement as far as the physical characteristics of the residues, the morphology of the individual particles, and the distribution of hemicellulose, cellulose, lignin and silica are concerned.

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References

1 Malaysian Agricultural Directory and Index 1993/94, Ministry of Agricultural, Kuala Lumpur, Malaysia.
2 I. A. Rahman, *J. Mater. Chem.*, 1992, **2**, 1107.
3 F. Adam, I. A. Rahman and M. I. Saleh, in *Seramik Nusantara*, ed. R. Othman, U.S.M. Penang, Malaysia, 1990, pp. 261–273.
4 M. A. Hamad, *J. Chem. Biotechnol.* 1981, **31**, 624.
5 TAPPI T6 revised: T 204 05, 1976.
6 L. E. Wise, E. J. Murphy and A. A. D'Addieco, *Paper Trade J.*, 1946, **122**, 35.
7 TAPPI T203, revised: T 203 05, 1974.
8 I. A. Rahman and F. L. Riley, *J. Eur. Ceram. Soc.*, 1989, **5**, 11.
9 I. A. Rahman, *Ceram. Inter.*, 1994, **20**, 195.
10 I. A. Rahman and M. I. Saleh, *Mater. Lett.*, 1995, **23**, 157.
11 J. G. Lee and I. B. Cuttler, *Am. Ceram. Bull.*, 1975, **54**, 195.
12 H. Hamdan and E. Listiorini, *Buletin Kimia*, 1994, **9**, 37.
13 K. Voshimichi, S. Kumio, S. Tsuneji, M. Fujio and S. Shigenitsu, *Chem. Express*, 1992, **7**, 521.
14 S. Tamin and I. Gurgey, *Chim. Acta Turc.*, 1988, **16**, 58.
15 H. Tanzil, T. Wahab and S. Zafar Ahmad, *Pak. J. Sci. Ind. Res.*, 1988, **31**, 221.
16 M. Cici and E. Keles, *Pak. J. Sci. Ind. Res.*, 1990, **33**, 347.
17 I. A. Rahman and J. Ismail, *J. Mater. Chem.*, 1993, **3**, 931.
18 M. Patel, A. Karera and P. Prasanna, *J. Mater. Sci.*, 1987, **22**, 2457.
19 W. Schnabel, *Polymer Degradation—Principles and Practical Applications*, Hanser International, Munich, Germany, 1981, p. 204.
20 J. James and M. S. Rao, *Thermochim. Acta*, 1986, **97**, 329.
21 P. Yang and S. Kokot, *J. Appl. Polym. Sci.*, 1996, **60**, 1137.
22 A. Basch and M. Lewin, *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 2035.

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