A physico-chemical study of husks of different varieties of rice grown in Sri Lanka

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NAXOS2018
13-16 June 2018

Varieties of rice husks investigated

- A traditional variety named as Black Heenati (BH) and ten other varieties bred at the Bathalagoda Rice Research Centre were investigated belonging to the Bg series of rice.
- All such varieties of rice were small rice grain types.

Bg 352

Black Heenati

Bg 300

Properties of rice husks investigated

Ash content of husks : Muffle furnace pyrolysis – 700 ^{0}C for 6h

Metals in husk : Atomic Absorption Spectroscopy

The precipitated silica from ash

Particle size distribution of precipitated silica

Scanning electron micrographs of precipitated silica

X ray diffraction study of precipitated silica

FTIR investigations of silica

Determination of lignin content in husk

Thermogravimetric and Differential thermogravimetric analysis of husks, silica and lignin

Ash content in different varieties of husks (%m/m)

Variety (Bg)	Heenati	352	300	360	359	358	94-1	366	357	379	406
% Ash	19.82	14.64	14.50	14.44	14.22	12.61	13.11	15.70	14.17	12.16	17.23

- Traditional Black Heenati variety recorded a much higher ash content of **19.82%.**
- The variation ranged from 12.16% -19.82% with an average ash content of **14.78%.**
- The most widely cultivated Bg 352 variety recorded an ash content of **14.64 %** which is near average value.

Metal content in husk (%m/m)

Variety	Na_2O	K_2O	MgO	CaO	MnO	CuO	ZnO	Fe_2O_3	As_2O_3	CdO
Heenati	0.295	0.540	0.651	0.111	0.193	0.002	0.011	0.051	5.0×10^{-4}	1.0×10^{-4}
Bg 352	0.256	2.099	1.086	0.342	0.224	0.004	0.014	0.079	2.0×10^{-4}	8.1×10^{-5}
Average of eleven varieties	0.271	1.524	0.948	0.357	0.210	0.004	0.013	0.112	1.0×10^{-4}	1.0×10^{-4}
AL Heenati	0.011	0.009	0.006	0.004	0.003	1.0×10^{-4}	0.001	0.006	6.1×10^{-6}	1.0×10^{-4}
AL Bg 352	0.011	0.009	0.025	0.010	0.004	4.0×10^{-4}	0.002	0.011	5.6×10^{-6}	1.0×10^{-4}

AL refers husks leached with 10% HCl for 2 hours, washed and dried prior to ashing

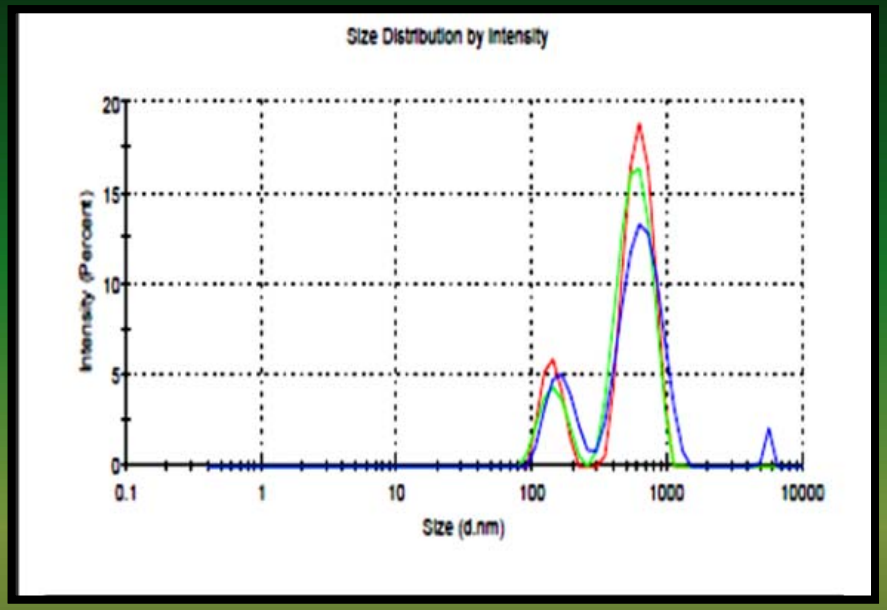
- Potassium and Magnesium were the main metals in the Bg series of rice varieties but was noticeably low in Black Heenati (BH) traditional variety.
- Although BH had the highest ash content, the total metal content is seen to be less than in all other varieties due to a higher silica content in this variety.
- Dangerous heavy metals such as As and Cd were only present in trace quantities.
- Metals in acid leached husks were very low.

The precipitated silica content

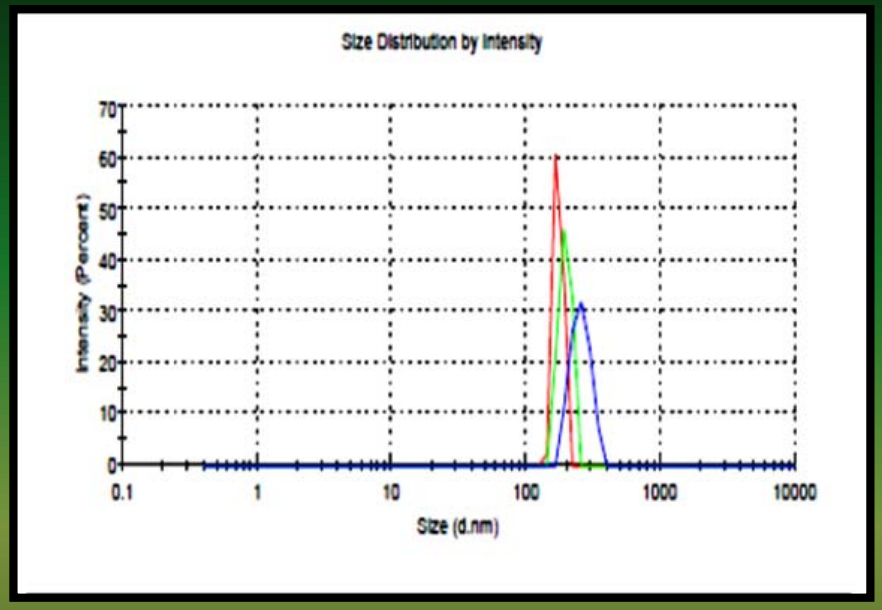
Variety (Bg)	Heenati	352	300	358	94-1	360	359	366	357	379	406
% Ash	19.82	14.64	14.50	12.61	13.11	14.44	14.22	15.70	14.17	12.16	17.23
% Silica on ash	93.15	95.89	96.52	95.44	95.46	96.39	93.61	95.22	93.43	96.06	95.04
% Silica on husk	18.46	14.03	14.00	12.03	12.51	13.91	13.31	14.95	13.24	11.68	16.38

- The percentage of silica precipitated from the ash ranged from **93.15% – 96.52%.**
- The traditional Heenat**i** variety recorded the **highest** amount of silica in husk.
- The average value of precipitated silica by mass of husk is **14.05 %.**

Particle size distribution of precipitated silica



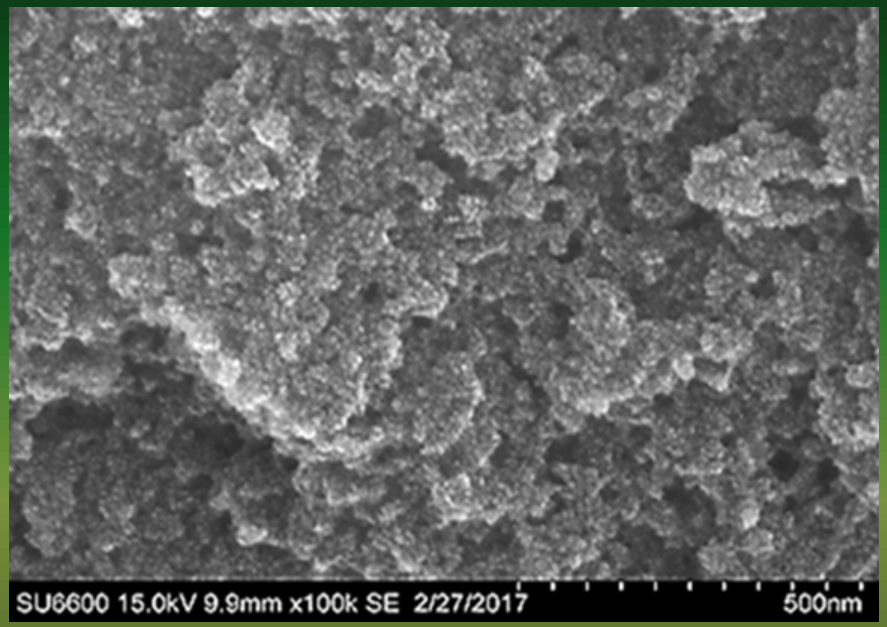
(a)
Particle size distribution of silica from un-leached Bg 352 husk



(b)
Particle size distribution of silica from leached Bg 352 husk

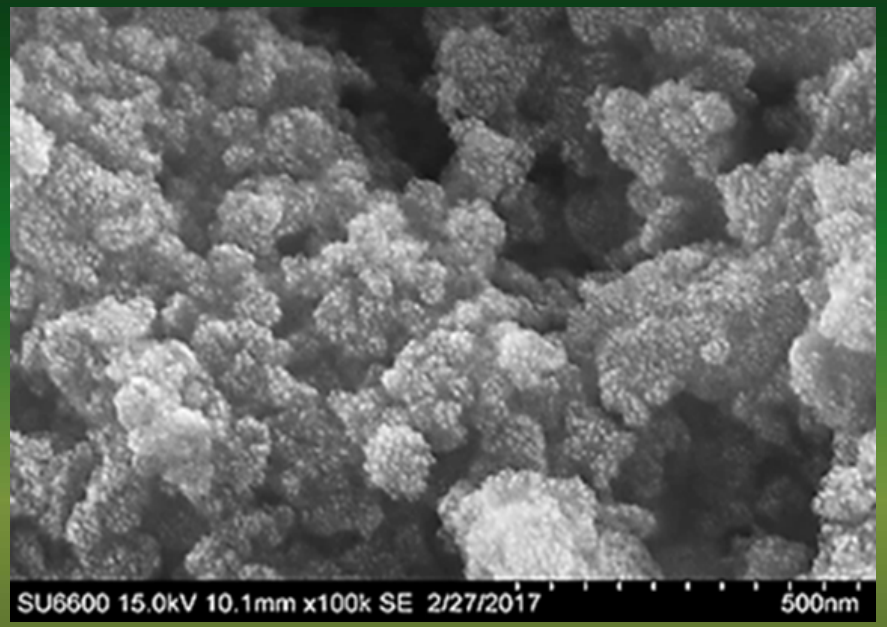
- Distributions were studied in triplicate and coincided well.
- Un-leached husks are seen to give a bimodal distribution with an additional small peak at very high particle size.
- Precipitated silica from leached husks showed a narrow single modal distribution.

Scanning electron micrographs of precipitated silica (mag x 100000)



(a)

Un-leached Bg 352 husk

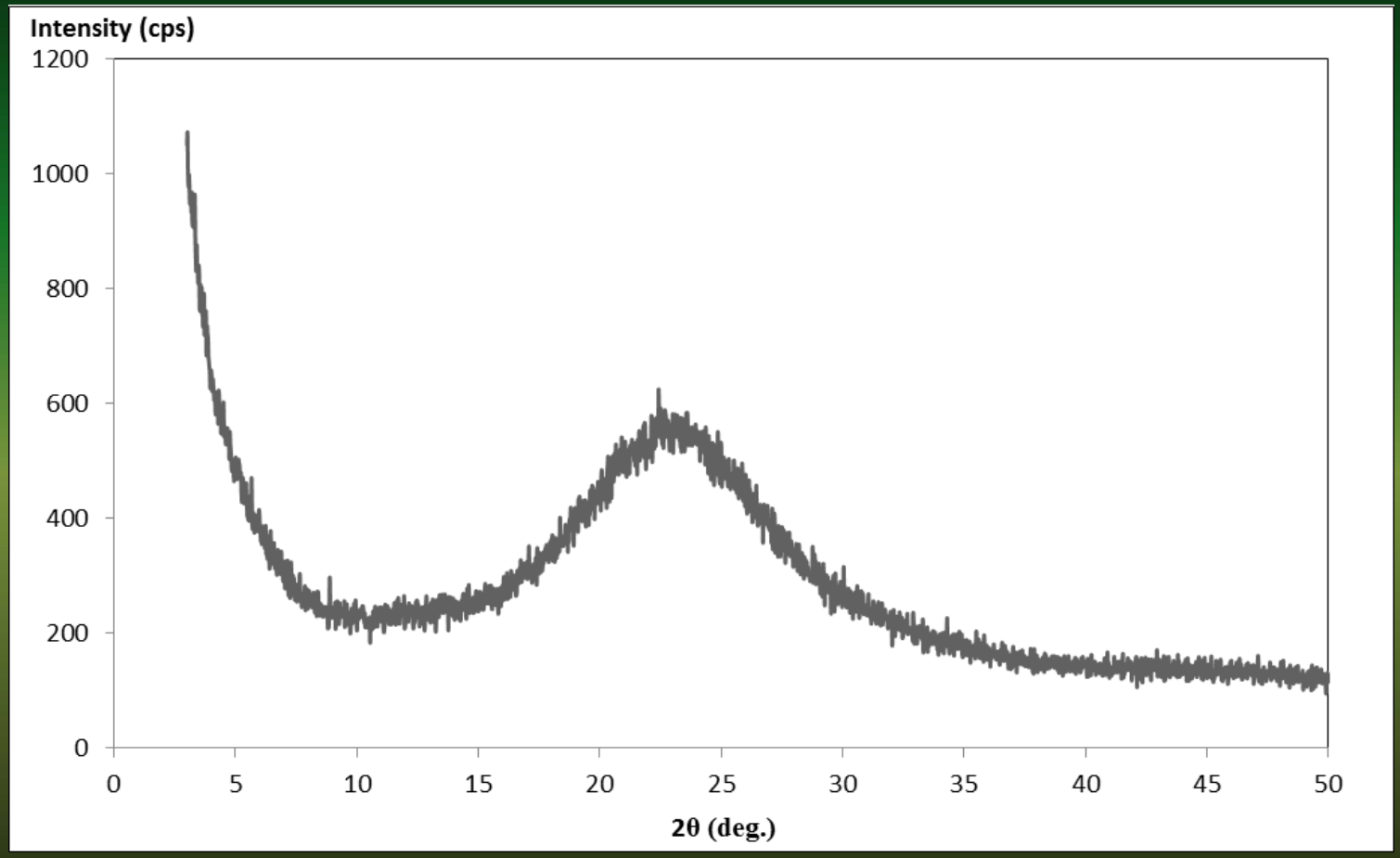


(b)

Acid leached Bg 352 husk

- Precipitated silica from un-leached husks are highly clustered where as that from leached husks have a much more open structure and the scale on the micrographs indicated individual clusters to be less than 500 nm.
- Individual clusters are seen to be much smaller individual particles.

XRD spectrum of precipitated silica



XRD spectrum of precipitated silica from un-leached husks of rice variety Bg 352

Material extracted from different varieties of husks by ASTM D 1106 – 96 (%m/m)

Variety (Bg)	Heenati	352	300	358	94-1	360	359	366	357	379	406
Material %	36.57	29.60	33.34	32.97	28.50	28.78	27.95	30.80	33.39	33.00	30.13

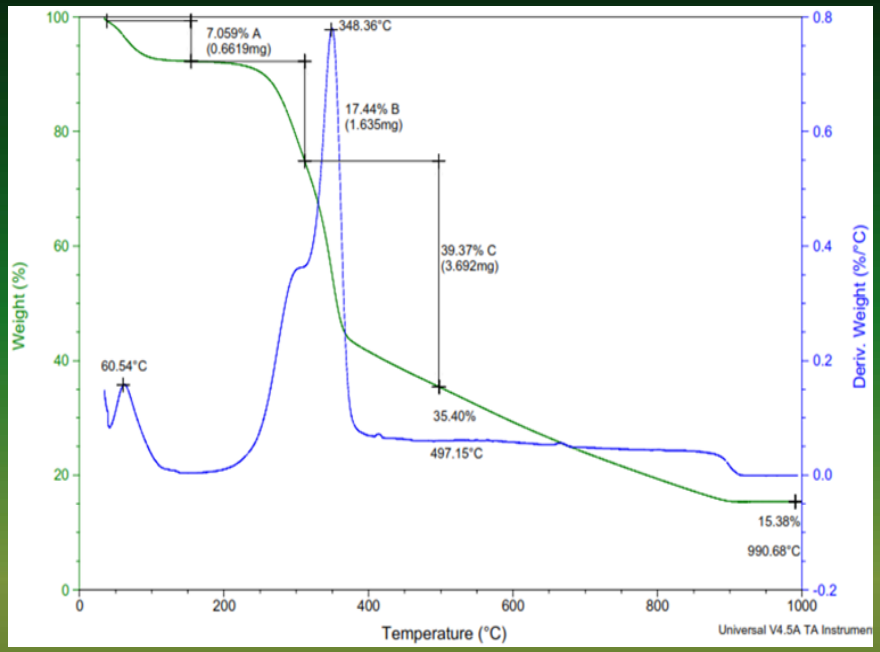
- Material extracted was chocolate brown in colour and ranged from **27.95% - 36.57**% by mass of husks.
- A traditional variety Heenati which had recorded the highest ash content is seen to record the highest extracted material as well.
- Further studies revealed the material to be a mixture of silica and lignin although the ASTM method used is to determine lignin content.

Determination of true lignin content in material extracted from Bg 352 husk by ASTM D 1106 -96 method

Material extracted by ASTM method	Actual silica content after pyrolysis at 700 ^{0}C for 6h	Actual lignin content after pyrolysis at 700 ^{0}C for 6h
29.63%	9.69%	19.91%

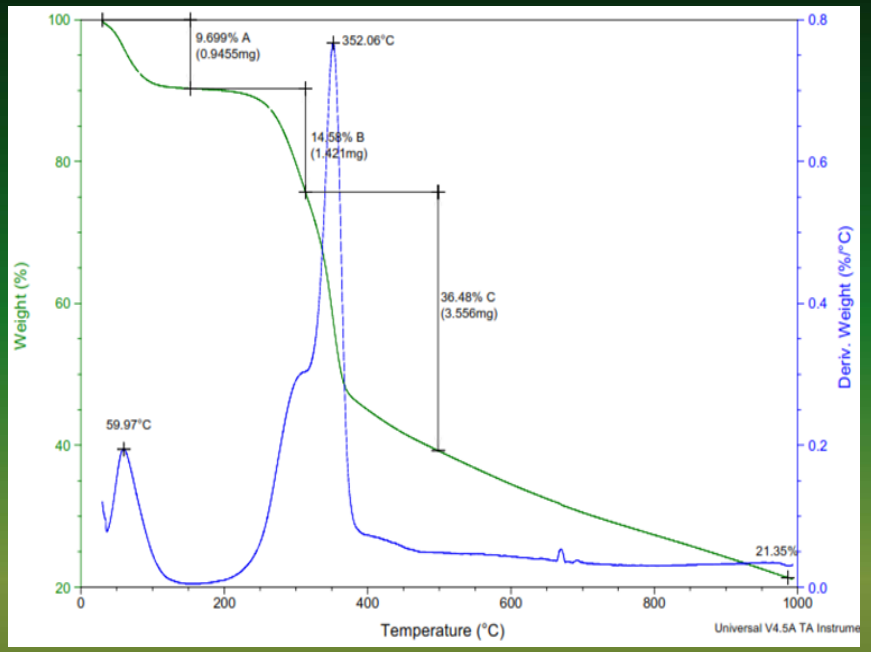
- 29.63% of mass of the husks of most popular variety Bg 352 was extracted as chocolate brown residue.
- On pyrolysis using a muffle furnace at 700 ^{0}C for 6 h, a white silica residue amounting to **9.69%** (32.74% of brown residue) remained.
- The pyrolysed amount of **19.91%** was determined to be the true lignin content of the husk.

TGA / DTG of varieties of husks Bg 352 and Black Heenati



(a)

TGA and DTG curves of husks of variety Bg 352

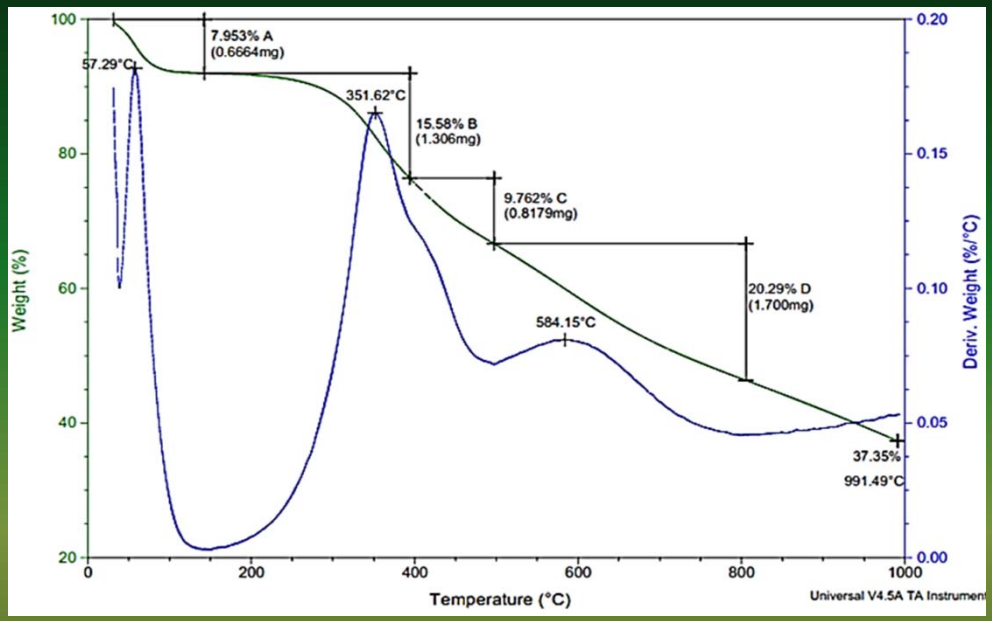


(b)

TGA and DTG curves of husks of Black Heenati variety

- Initial DTG peak corresponds to a moisture loss up to a temperature < 150 degrees.
- The twin DTG peak corresponds to pyrolysis of hemicellulose and cellulose.
- Beyond 400 ^{0}C, the rate of pyrolysis is constant and corresponds to that of mainly lignin.
- Unpyrolysed residue at 1000 ^{0}C in Bg 352 was 15.38 % and that of Black Heenati, it was 21.35% due to a higher silica content which was also seen the highest ash determination.

TGA/DTG of material extracted by ASTM D 1106-96 from Bg 352 husk



TGA and DTG curves of material extracted from Bg 352 husks by ASTM D 1106 - 96 method

- Moisture content is seen to be 7.953%.
- DTG shows a prominent peak at 351^{0}C but the rate of pyrolysis is only 0.175% mass %/^{0}C of the extracted material which was only 29.6% of the mass of husks. Therefore the pyrolytic peak of lignin if expressed as rate of pyrolysis on mass of husks is a very low rate compared to the high rate of pyrolysis of the cellulose peak at the same temperature which was close to 0.8% of the husk. Therefore the lignin peak is hidden in the cellulose peak of the husk.

The chemical composition of rice husk of Bg 352

Ingredients	% Composition
Volatile matter	7.06
Ash	14.6
Silica in husk	9.69
Metal oxides in ash	4.95
Lignin in husk	19.91
Hemicellulose /Cellulose (by difference)	58.39

Hemicellulose and cellulose content = 100 – (Volatile matter + Ash + lignin)

TGA of Bg 352 indicates a mass drop of 17.44% from 200 ^{0}C to 300 ^{0}C and this mass loss corresponds to pyrolysis of hemicelluloses as cellulose is thermally stable up to 300 ^{0}C. Since hemicelluloses are known to pyrolyse slowly to much higher temperature, it is reasonable to estimate hemicelluloses to be about 22% of mass of husks. If so, the cellulose content is about 36.39%. Therefore cellulose content in husk is very high.

Conclusions

- This study gives a fuller understanding of variety based physico-chemical properties of husks and a high percentage of industrially valuable materials such as silica and lignin are extractable.
- The chemical composition of husk is presented in table form indicating the moisture, ash comprising of silica and metal oxides, lignin and estimated hemicelluloses and cellulose.
- A novel method of determining lignin content was found by pyrolysing the extracted material using ASTM D 1106 – 96 method.
- There is further scope for research using high percentage of silica and lignin extractable as reinforcing materials in the rubber industry.
- Metal analysis in husks shows it to be a friendly material carrying only trace amounts of toxic metals.

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Thank You