Chemi-mechanical Pulping of Durian Rinds

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Abstract

The physical, optical and mechanical characteristics of pulp and paper made from waste durian rinds as an alternative raw material for papermaking were investigated according to TAPP I and MS ISO standards. The durian rinds pulp was produced through chemi-mechanical pulping (CMP). Naturally dried durian rinds were treated with 10% Sodium Hydroxide (NaOH) based on oven dry (o.d) weight of durian rinds in room temperature for 2 hours and pulped by the refiner mechanical pulping (RMP) process. Experimental results show that durian rinds have great potential characteristics as newly explored non-wood based raw material for pulp and paper industry.

Keywords: Durian rinds; Chemi-mechanical pulping (CMP); Pulp; Paper

1. Introduction

Paper is one of the required high demand materials in the market although the paperless technology has been proposed. Paper is mostly used in printing operations such as money, books, newspapers and also packaging work such as food packaging, wrapping and other things more in daily use. The increasing demand of wood based material for papermaking is indirectly increase the deforestation activities and also affect the harmful to the environment. The continuous usage of wood as a raw material in papermaking industry will affect the ecosystem of
the forest and also further will affect the economic potential against highly limited wood resources available. Some studies have been carried out to find the other best solutions to replace wood with the non-wood raw materials such as oil palm empty fruit bunch (EFB) [1–4], oil palm male flower [5], kenaf [6], pineapple leaf [7], bagasse [8-9], coir fiber [10-11] and banana fiber [12]. Besides, there was less research on usage of durian rinds for paper pulp.

Durian (Durio Zibethinus Murr) is also known as the "King of Fruits". Durian is the most popular fruit in Southeast Asia. According by Lim and Luders [13], durian is famous by its taste and smell delicious by most Asians but for most Western people, they do not like durian because of its smells was very bad. Durian rinds always be dumped and abandoned after the arils have been harvested. Only one-third of durian is edible, whereas the seeds (20–25%) and the shell are usually thrown away [14]. Aril, the edible portion of the fruit only accounts for about 15–30% mass of the entire fruit [15]. Therefore, approximately 70 – 85% of the durian fruit is discarded as waste materials and would be an environmental problem if not disposed in a proper manner [16]. To avoid the pollution effected by the dumping of durian rinds on the environment, this waste material will be investigated as an alternative non-wood raw material in producing paper in this study. Table 1 shows the chemical composition analysis results for durian peel and fiber as reported by previous study [17–19]. It can be seen that durian peel and fiber contains lignin and hemicelluloses which is the primary cause of the change in the characteristics of the natural fibers in papermaking. It can be seen that durian peels have rich hemicellulose content. Hemicellulose is the difference between holocellulose and cellulose. Moisture content, ash content, carbon content and oxygen content for the durian shell is 11.27%, 4.84%, 39.3% and 53.74%, respectively as reported by Jun et al. [20].

The objective of this study is to investigate the characteristics of paper made from 100% of durian rinds with chemi-mechanical (CMP) pulping process. Overall pulp and paper characteristics test were conducted according to Technological Association of the Pulp and Paper Industry (TAPPI) and Malaysia ISO (MS ISO) standards. This study was conducted to provide a new alternative non-wood based raw material for pulp and paper industry. The application of durian rinds as an ingredient in the production of paper instead usually being thrown away after the aril was taken could indirectly benefit the durian industry.

Table 1. Chemical composition of durian peel and durian fiber [17–19]

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Standard</th>
<th>Dried durian peel (%)</th>
<th>Dried Durian peel fiber (%)</th>
<th>Durian peel (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash Content</td>
<td>TAPPI-T211-om-93</td>
<td>5.5</td>
<td>4.3</td>
<td>4.35</td>
</tr>
<tr>
<td>Alcohol-benzene-solubility</td>
<td>TAPPI-T204-om-93</td>
<td>13.4</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>Ethanol-benzene-Solubility</td>
<td>TAPPI-T204-cm-97</td>
<td>-</td>
<td>-</td>
<td>16.65</td>
</tr>
<tr>
<td>Ethanol-solubility</td>
<td>TAPPI-T264-cm-97</td>
<td>15.5</td>
<td>18.6</td>
<td>13.09</td>
</tr>
<tr>
<td>Lignin (ash corrected)</td>
<td>TAPPI-T222-om-98</td>
<td>10.9</td>
<td>10.7</td>
<td>15.45</td>
</tr>
<tr>
<td>Holocellulose</td>
<td>Acid Chlorite’s Browning</td>
<td>47.1</td>
<td>54.2</td>
<td>73.54</td>
</tr>
<tr>
<td>α-cellulose</td>
<td>TAPPI-T203-cm-88</td>
<td>31.6</td>
<td>35.6</td>
<td>60.45</td>
</tr>
<tr>
<td>Hemi-cellulose</td>
<td>-</td>
<td>15.5</td>
<td>18.6</td>
<td></td>
</tr>
</tbody>
</table>

2. Methodology

2.1. Raw material preparation

The waste durian rinds were collected from local farm at Batu Pahat, Johor, Malaysia after the arils were taken away. Fresh durian rinds were cleaned from any dirt and residual aril under running water. Durian rinds were sliced in 5-10 mm of thickness. Then, the durian rinds spikes need to be removed. After that, the rinds were cut into small cube in shape pieces with approximately size of 5-10 mm for width, length and depth as Fig.1 (a) and Fig. 1(b). Finally, the durian rinds cubes were naturally dried directly under the sunlight for about 2 - 3 days. The air dry (a.d.) durian rinds as Fig. 1(c) were stored in close air tight container at room temperature to prevent from fungus.
2.2. Chemi-mechanical pulping

Pulping is the important process to produce durian rinds pulp in papermaking. In this research, durian rinds pulp were produced by chemi-mechanical pulping process according to the control conditions as shown in Table 2.

Table 2. Chemi-mechanical pulping conditions of durian rinds

<table>
<thead>
<tr>
<th>Pulping conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active alkali- NaOH (%) based on oven dry (o.d) weight</td>
<td>10%</td>
</tr>
<tr>
<td>Time for NaOH treatment (hr)</td>
<td>2 hours</td>
</tr>
<tr>
<td>Liquor to raw material ratio</td>
<td>6:1</td>
</tr>
</tbody>
</table>

2.2.1. Moisture content analysis

Durian rinds moisture content was determined by the moisture analyzer (Fig. 2) for faster result. Approximately, 2 g of naturally air dry of durian rinds required to measure the moisture content. The moisture analyzer used to determine the moisture content of durian rinds in order to get faster results. To validate the results from moisture analyzer, durian rinds moisture content was once again determined by oven drying method according to Malaysian Standard MS ISO 287 : 1985, IDT. Hence, 2 set of measurements were conducted to determine more accurate value of the durian rinds moisture content.

2.2.2. Sodium hydroxide treatment

The weight of Sodium Hydroxide (NaOH) was determined 10% from the oven dry (o.d) weight of durian rinds. After that, NaOH tablets were stirred in 2 liters of water by magnetic stirrer. Then, 1980 g air dry (a.d.) weight of dried durian rinds were soaked according to 1:6 oven dry (o.d.) fibers to liquor ratio for 2 hours in room
temperature. Finally, After 2 hours of NaOH treatment, the durians rinds were washed with running water and screened to removes water.

2.2.3. Refiner mechanical pulping

The treated durian rinds (DR) were refined into pulp by using Refiner Machine Pulping (RMP) machine located at Forest Research Institute of Malaysia (FRIM) as shown in Fig. 3(a). The durian rinds were poured into the entrance of RMP and then the screw press will send the durian rinds into the refiner blades. The water hose was connected into the entrance of the refiner blade to make sure the process flow smoothly. Water containing refined durian rinds flows down along the aluminum base outlet. Finally, the refined durian rinds were filtered out by a screening container to remove water and undersized debris as shown in Fig. 3(b) and Fig. 3(c).

![Refiner Mechanica Pulping Machine (RMP); (b) Refined durian rinds screening; (c) Refined durian rinds](image)

Fig. 3. (a) Refiner Mechanical Pulping Machine (RMP); (b) Refined durian rinds screening; (c) Refined durian rinds

2.2.4. Screening

After the RMP process, the screening process undergo by using PTI Sommerville Fractionators according to TAPPI T 275 standard with slot size of 0.15 mm. The oversized debris particles from durian rinds pulp such as durian spikes were screened out. Finally, the pulps with size of 200μ-250μ were screened out by a screening container to remove water.

2.2.5. Spin Drying

Durian rinds screened pulp were spin-dried to remove as much residual water by using spinning machine as shown in Fig. 4(a). The screened pulps were placed inside a fabric bag. Then, the pulps were spin-dried for 5 minutes. After spinning process was completed, the pulps were poured into the Hobart Mixer as Fig. 4(b) to dissolve the pulp. Then, the durian rinds CMP pulp in Fig. 4(c) was weighted to determine the pulp yield percentage. Finally, the pulp was stored inside the freezer at 6 °C as shown in Fig. 4(d).

![Spin dryer; (b) Hobart mixer; (c) Durian rinds CMP pulp; (d) Storage chiller](image)

Fig. 4. (a) Spin dryer; (b) Hobart mixer; (c) Durian rinds CMP pulp; (d) Storage chiller
2.3. Paper sheet preparation

The laboratory paper was made by a semi-automatic sheet machine (British Handsheet Machine) according to TAPPI T 205 om-88 Forming Handsheets for Physical Tests of Pulp. 24 g of free moisture content pulp required to produce overall test sample according to 60 gsm paper. Firstly, pulps were disintegrated to disperse the bundled pulp. 2 liters of water were added into the disintegrator tank contain with the pulp and run for 2000 revolutions. After completion, the disintegrated pulps were poured into the stock divider. Water level inside the stock divider was raised up to 8 liters level. Pneumatics air bubble used to mix the pulp and water evenly.

The freeness test was conducted according the TAPPI T 227 om-99: Freeness of Pulp (Canadian Standard Method). 2 sets of freeness diluted pulp (1 liter of diluted pulp per set) were taken out from the stock divider to perform the freeness test by a freeness test apparatus. After completion, the same 2 sets of freeness pulp were used to produce paper sheets by a sheet former. The two pieces of freeness paper sheet were dried in the oven at 105°C to determine the freeness correction value. After the 2 sets of freeness sample were taken out from the stock divider, the water then was added again until it reached 14 liters level.

2 sets of correction sample (1 liter of diluted pulp per set) were taken out from the stock divider. Correction test must be performed to check the weight of the paper sheet is over or lower than as standard weight. 2 pieces of correction paper sheet were produced by paper sheet forming process. The paper sheet then dried using the rapid flat dryer at 105°C. For 60 gsm paper, the standard weight was 1.22 g. Water was reduced from the stock divider if the weight of the correction paper is lower than the standard. Besides, water is added if the weight of paper is over than the standard. Air bubble in the stock divider must be closed and pulp must be left for about 20 minutes if the water needs to be reduced.

The remaining 12 liters of diluted pulp inside the stock divider used to produce the testing samples after the correction procedure has been done. Hand sheet former is an apparatus to produce a paper sheet consists of a complete sheet machine, perforated stirrer, couch roll, couch plate and a grid plate as shown in Fig. 5(a). From the stock divider that contains of 12 liters diluted pulp, it can produce into approximately 12-13 pieces of testing samples. Sheet making procedure was started by turn on the water while the sheet machine was open to remove any adhering fibers. 1 liter of diluted durian rinds pulp was poured into the sheet machine cylindrical deckle after the sheet machine was closed and filled with half of water. Water was added until it reached the line level inside the sheet machine. The perforated stirrer was inserted into the sheet machine and moved upward and downward for about 5 times to uniformly mix the slurry. The drainage time is taken by a stopwatch when the water outlet valve is release rapidly. After the water drained out under suction by opening the water valve rapidly, only a drained sheet was left on the wire screen as shown in Fig. 5(b). The drainage time is stopped after water is fully drained. 2 pieces of blotter paper were placed on the centre of the paper sheet and a couch plate is placed centrally on the blotter papers. The couch roller is rolled forwards and backwards on the centre of the plate without any pressure for 3-5 times to remove residual water contain and make the paper sheet attached on the couch blotter paper as Fig. 5(c). After completion, all paper sheet samples must be pressed uniformly with press machine in order to make sure the sample in a flat shape and also removes the residual water content. Each paper sheet sample attached to the couch blotter were placed on the 2-3 pieces of dry blotter and covered by a polished plate on the top of it located to the centre of the press machine flat base by using a guide as shown in Fig. 5(d). The samples were pressed approximately at 345 kPa of pressure for about 5 minutes. After changing the blotter paper between paper sheets, the pressing procedure was repeated for another session with same pressure and time.

![Fig. 5. (a) Paper sheet former (b) fiber sheet (c) paper sheet on blotter paper (d) press machine](image-url)
The paper sheets that attached to the polished steel plate were fixed above and below to the stack of standard drying rings to make sure the paper is dried in flat condition as shown in Fig. 6(a). A heavy weight was placed at the top of the drying ring to give the pressure to the edge of paper sheets and make the sample dried uniformly inside a control room with temperature of (23.0±1°C), and of (RH=50.0±2%) for at least 24 hours. After 24 hours of drying process, the sample is take out from the drying ring and conditioned inside the control room with temperature of (23.0±1°C), and of (RH=50.0±2%) for another 12 hours as shown in Fig. 6(b) and Fig. 6(c).

2.4. Characteristics test

The structural, mechanical and optical properties were in a controlled temperature and humidity environment as stipulated in TAPPI T 402 om-93 Standard Conditioning and Testing Atmospheres for Paper, Board, Pulp Handsheets and Related Products and MS ISO 187: 1990, IDT. The sampling was conducted according to MS ISO 186: 2002, IDT. The weights of each 60 gsm of durian rinds CMP paper sheet sample were determined. From the weight obtained, paper sheet with the highest and lowest weight were pulled out. The physical and optical tests that were conducted such as grammage (MS ISO 536 : 1995, IDT), thickness (MS ISO 534: 2005, IDT), brightness test (MS ISO 2470-1: 2009, IDT : Standard of Paper, Board and Pulps – Measurement of Diffuse Blue Reflectance Factor), and opacity test (MS ISO 2471: 2008, IDT : Determination of Opacity (Paper Packing – Diffuse Reflectance Method), For the testing samples, the best eight of paper sheets samples were selected to be tested. After the physical and optical characteristics tests were completed, each durian rinds paper sheet as Fig. 7(a) were cut according to the dimensions shown in Fig. 7(b) for the mechanical characteristics test. The mechanical tests that were conducted are tensile test (MS ISO 1924-2 : 2008, IDT : Paper and Board – Determination of Tensile Properties – Part2 - Constant Rate of Elongation Method), tearing test (MS ISO 1974 : 1990, IDT : Paper – Determination of Tearing Resistance - Elmendorf Method), bursting strength (MS ISO 2758: 2001, IDT : Paper-Determination of Bursting Strength) and folding test (MS ISO 5626 : 1993, IDT : Paper – Determination of Folding Endurance). For grammage test, overall specimen after the tearing test (16 pieces) were placed into the oven for not less than 30 minutes at temperature of 105°C as referred to MS ISO 287: 1985, IDT to remove moisture content.
3. Results and discussions

3.1. Durian rinds moisture content

In this research, 1980 g air dry (a.d.) weight of naturally dried durian rinds was prepared for pulp preparation. With moisture analyzer, moisture content of the fiber recorded a value of 14.61 %. This value is quite higher than 11.27% as reported by Jun et al. [20]. It means, 85.39% or 1691 g of moisture free content was inside the 1980 g of durian rinds. Oven dry method determined that moisture content of durian rinds shows average result of 9.825 %. It means, 90.175 % of moisture free content was inside the durian rinds. This value is lower than 11.27% as reported by Jun et al. [20]. This may due from the climate condition in Malaysia and different method of drying process.

3.2. Durian rinds pulp properties

In this research, within the 1980 g weight of durian rinds, 90.175 % or 1785 g of oven dry weight starting material used for pulp preparation. 5070 g of air dry (a.d) durian rinds pulp was produced after refining mechanical pulping (RMP) and screening process. Moisture content result of the durian rinds pulp was 82%. So, there are only 18% or 912.6 g of moisture free content inside the durian rinds pulp. It was calculated that the durian pulp screened yield is about 51.11 %. The yield percentage of screened durian rind pulp by chemi-mechanical pulping process is quite lower compared to common yield of chemi-mechanical pulping process is about 55 % - 85 %. Unbeaten CMP durian rinds pulp recorded the Kappa number of 100 which is very high lignin content. This number shows how much lignin content in durian rinds pulp for papermaking. This value can be reduced by bleaching process or chemical pulping process. Corrected freeness value shows that CMP durian rinds pulp only can achieved freeness value of 89. Table 3 shows the durian rinds CMP pulp holds the water content that absorbed inside the pulp.

Table 3. Durian rind CMP pulp characteristics

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Moisture content (%)</th>
<th>Screened Yield (%)</th>
<th>Kappa Number</th>
<th>Klassen Lignin (%)</th>
<th>Freeness (corrected)</th>
<th>Drainage time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>82 %</td>
<td>51.11 %</td>
<td>100</td>
<td>13 %</td>
<td>89</td>
<td>74</td>
</tr>
</tbody>
</table>

3.3. Physical properties

The objective of the grammage test is to determine the weight of paper per unit area and expressed in grams per square meter (g/m²) or called as gsm. The objective of the experiment is to get the standard basis weight of 60 gsm. The results recorded the grammage which is 58.87 g/m² was quite similar with the value of standard target of 60 gsm paper grammage as shown in Table 4. Durian rinds paper shows a value of 128.59 μm for bulk thickness in Table 4. Apparent density is one of the most significant properties of paper and influences almost all mechanical, physical, and electrical properties [4]. Table 5 shows that durian rinds paper has compatible bulk density compared to old carton box, old newspaper and old copier paper reported by Ibrahim [2] and Rushdan et al. [4].

Table 4. Durian rinds CMP 60 gsm paper sheet physical characteristics

<table>
<thead>
<tr>
<th>Pulp</th>
<th>Grammage (g/m²)</th>
<th>Bulk Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durian rinds CMP Pulp</td>
<td>58.87</td>
<td>128.59</td>
</tr>
</tbody>
</table>

Table 5. Durian rinds CMP 60 gsm paper sheet pulp bulk density result comparison

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.46</td>
<td>0.67</td>
<td>0.48</td>
<td>0.48</td>
<td>0.41</td>
<td>0.40</td>
<td>0.49</td>
<td>0.54</td>
</tr>
</tbody>
</table>
3.4. Mechanical properties

Tensile index, tearing index, bursting index and folding were the most important characteristics of paper. Table 6 shows the mechanical characteristics of paper made from chemi-mechanical (CMP) durian rinds pulp. Durian rinds paper sheet tensile index, tearing index, bursting index and folding number shows value of 34.67 N.m/g, 4.918 mN.m²/g, 1.86 kPa.m²/g and 1.18 respectively. Durian rinds paper shows better value in tensile index, tearing index and double fold number compare to coir paper [11] except tearing index. These conditions may be enhanced by bleaching and beating process.

Table 6. Mechanical characteristics of durian rinds CMP paper

<table>
<thead>
<tr>
<th>CMP pulp properties</th>
<th>Durian rinds CMP</th>
<th>Coir CMP [11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Index (Nm/g)</td>
<td>34.67</td>
<td>18.33</td>
</tr>
<tr>
<td>Tearing index (mN.m²/g)</td>
<td>4.918</td>
<td>7.050</td>
</tr>
<tr>
<td>Bursting Index (kPa.m²/g)</td>
<td>1.86</td>
<td>1.85</td>
</tr>
<tr>
<td>Double Folding No.</td>
<td>15.00</td>
<td>8.07</td>
</tr>
</tbody>
</table>

3.5. Optical properties

Table 7 shows unbleached durian rinds CMP paper recorded ISO Brightness and ISO opacity value of 13.20% and 97.73% respectively. Durian rinds unbleached CMP paper sheet shows ISO brightness and ISO opacity lower than coir CMP unbleached paper [11]. This is due to durian rinds pulp have more lignin content based on higher Kappa Number than coir paper [11] in Table 7. In the future, bleaching process will be taken as consideration to enhance the optical characteristics of durian rinds paper by reducing the lignin content.

Table 7. Durian rinds CMP paper optical characteristics

<table>
<thead>
<tr>
<th>Properties</th>
<th>Durian rinds CMP unbleached</th>
<th>Coir CMP (unbleached)[11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO Brightness (%)</td>
<td>13.20</td>
<td>16.83</td>
</tr>
<tr>
<td>ISO Opacity (%)</td>
<td>97.73</td>
<td>99.60</td>
</tr>
<tr>
<td>Kappa Number</td>
<td>100</td>
<td>86.87</td>
</tr>
</tbody>
</table>

3.6. Scanning Electron Microscopy (SEM)

Durian rinds fiber paper surface morphology was investigated by using Scanning Electron Microscopy. By using the SEM image for unbleached and unbeaten durians rinds paper and unbleached durian rinds paper were examined. Fig. 8(a) shows the top image in 100 x magnification of unbleached and unbeaten paper made from durian rinds obtained from SEM. Fig. 8(b) shows the top surface of unbeaten durian rinds paper in 500 x magnifications. It can be seen that fiber arrangement and binding was not so uniform. The fiber arrangements were not straight and have some kinks and crimps. Side cross section of durian unbleached and unbeaten rinds paper in Fig. 8(c) shows that the arrangement was not so dense. Interfiber bonding and fiber individual strength were the important factor in paper characteristics. In future study, this condition may be improved by the beating and bleaching process.
Fig. 8. (a) Top SEM image in 100x magnification of unbleached and unbeaten durian rinds paper (b) Top SEM image in 500x magnification of unbleached and unbeaten durian rinds paper (c) Side image 500x magnification of unbleached and unbeaten durian rinds paper

Fig. 8 shows there are pit holes along durian fiber on the paper made from unbeaten durian rinds fiber. These holes are commonly appearing from the natural fiber especially from the plants and animal. The measured pit holes sizes are 1.193μm, 1.671 μm, 2.059 μm, 1.366 μm, 1.492 μm, 1.703 μm and 1.681 μm as shown in Fig. 9(b).

Fig. 9(a) shows there are pit holes along durian fiber on the paper made from unbeaten durian rinds fiber. These holes are commonly appearing from the natural fiber especially from the plants and animal. The measured pit holes sizes are 1.193μm, 1.671 μm, 2.059 μm, 1.366 μm, 1.492 μm, 1.703 μm and 1.681 μm as shown in Fig. 9(b).

4. Conclusion

Pulp and paper from durian rinds were successfully produced in this research. In the other hand, optical, physical and characteristics of chemi-mechanical pulp of durian rinds were also successfully investigated in this study. The characteristics results show some promising potentials of durian rinds as a newly explored raw material for papermaking but still need to be improved. For better results, beating and bleaching process should be taken as consideration as beating and bleaching may enhanced the durian rinds pulp and paper characteristics. The increment of NaOH percentage treatment also may enhance the interfiber bonding and individual strength of the paper. Another type of pulping such as chemical Soda-AQ and kraft pulping should be considered. As a conclusion, the research findings shows that durian rinds could offer future investigations about this non-wood based raw material and have great potentials to be applied as newly explored raw material for pulp and paper industry.
5. Acknowledgement

The author would like to thank Universiti Tun Hussein Onn Malaysia for funding this project under UTHM Short Term Grant (STG) Vot. 1333 and Ministry of Education Malaysia under SLAI scheme. Author would also like to acknowledge Forest Research Institute of Malaysia (FRIM) for research facilities and support.

6. References