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# STUDIES ON SODA-SULPHUR PULPING

## Part I. Pulping of Rice-straw (*Oryza sativa*) by Soda-sulphur Process

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A stronger pulp with higher yield is obtained by use of soda-sulphur process on rice-straw (*Oryza sativa*). The pulp thus produced can be used for production of good quality writing and printing paper.

*Key words:* Soda-sulphur, Pulping, Rice-straw.

## INTRODUCTION

Rice-straw, an agricultural waste contains a substantial amount of cellulose. Rice-straw is therefore available in large quantities. Rice plant is widely cultivated in other tropical countries of the world alongwith Bangladesh.

Rice-straw is mainly used as cattle-feed and by villagers as fuel and roofing materials for their houses.

The present studies are based on rice-straw of aman variety though other varities like aus, boro and irri are also available. The analysis of rice-straw was carried out by Tappi standard methods [1-4] and reported in previous paper [5].

Different pulping techniques and pulping agents [6-11] were used on rice-straw from time to time. But no report was available regarding the application of soda-sulphur process on rice-straw. The use of sodium carbonate and sulphur was suggested for the preparation of coarse pulp for corrugating paper [12].

## EXPERIMENTAL

*Preparation of the raw material.* Rice-straws were sun-dried and cut into pieces of 1" in lenght. Moisture-content of the material was determined by keeping the samples in an electric oven at 105°.

*Preparation and analysis of cooking liquor.* The cooking liquor for soda-sulphur process was prepared by adding elemental sulphur to the pre-analysed caustic soda solution. by conventional method [13] for sodium hydroxide, sodium carbonate, etc. Analysis for elemental sulphur was carried out by Tappi procedures [14].

*Digestor.* A rotary digestor of stainless steel was used for pulping rice-straw.

*Determination of pulp-yields.* The yields for both unbleached and bleached pulps were determined by keeping portions of the pulps (each weighing 10 g over dry basis) in an electric oven at 105° for 18 hours.

*Determination of permaganate number.* The permaganate number was determined by Tappi procedures [15].

*Preparation of handsheets.* Standard handsheets each weighing 60g/M$^2$ were made from both unbleached and bleached pulps in rapid köthen sheet forming machine and conditioned according to Tappi standards [16, 17].

*Measurement of physical properties.* The brightness [18], breaking length [19], tear factor [20], burst factor [21] of both unbleached and bleached handsheets were determined by Tappi standards.

*Laboratory evaluation of unbleached and bleached pulps.* One kilogram each of oven dry basis of unbleached and bleached pulps were disintegrated and beaten according to Tappi standards [22] in pilot plant Hollander beater for a period of 60 min. Samples of pulp-slurry at the beginning of experiment and after every 10 min. interval of time were collected. Standard pulp-sheets were made from different collected samples and the sheets were tested as mentioned.

*Freeness.* The freeness of unbleached and bleached pulps was determined by Tappi standards. [23].

*Preparation and analysis of chlorine water.* Chlorine required for the first stage of multistage bleaching of pulps was prepared by oxidising hydrochloric acid with potassium permanganate and dissolved in water and analysed according to Tappi standard [24].

*Preparation of sodium hypochlorite solution and its analysis.* The sodium hypochlorite was prepared by passing chlorine gas into a cold solution of 2.0% sodium hydroide and analysed by Tappi method [24].

*Fibre-length and diameter.* These were done by Tappi standard [25].

*System of bleaching.* 3-stage bleaching system (CEH) and 5-stage system (CEHEH) were followed.

*Conditions of bleaching.* In CEH system, C stands for chlorination where 60% chlorine was supplied at 3.5%

consistency, pH 1-2, room temperature 25-30° for 1 hour and the remaining 30% chlorine was supplied as NaOCl during H-means sodium hypochlorite treatment at 3.5% consistency, pH 9-11, room temperature 25-30° for 1 hr. The intermediate step was (E) (caustic extraction) (2% against pulp o, b basis) for 1 hr. at 13.5 % consistency and temperature 75-80°.

In CEHEH system, C stands for chlorination where 60% chlorine was supplied and out of the remaining 30%, 15% was supplied during first (H) first sodium hypochlorite treatment and another 15% was supplied during second (H) second sodium hypochlorite treatment. Other conditions of CEHEH remained unaffected as those in CEH.

## RESULTS AND DISCUSSION

The percentage of pulp-yields of unbleached, CEH and CEHEH bleached soda-soulphur pulp of rice-straw were 57.94, 51.00 and 49.05 respectively (Tables 1-5 and 10). These values are higher than those obtained by others [5, 10, 11]. The different pulp-yields and amount of alpha-cellulose (36.05%) originally present in rice-straw showed that there was no abnormal loss during pulping and the loss was minimum with soda-sulphur pulp compared to soda pulp [5] of rice-straw.

The pulp-yields (57.94%) was obtained with the addition of 1.0% elemental sulphur to the cooking liquor (Table 2). Attempts for higher yield with additional amount of sulphur were unsuccessful. Therefore 57.94% was considered the highest pulp-yield obtained.

The reaction mechanism after the addition of elemental sulphur to the cooking liquor can be represented as follows.

$$6NaOH + 4S \longrightarrow 2\,Na_2S + Na_2S_2O_3 + 3H_2O$$

$$Na_2S + H_2O \rightleftharpoons NaOH + NaHS$$

Thus formation of sodium sulphide increases sodium hydroxide content of the cooking liquor. More significant

Table1. Effect of caustic soda on pulp-yield and permaganate number of the unbleached pulp and physical properties of the unbleached pulp-sheets from soda-sulphur pulp of rice-straw

(a) Material taken in g.o.d. basis 1000 (b) % sulphur 1.0 (c) Temperature °C 150 (d) Time in hours including 50 minutes to reach the temperature 2.5 (e) Material : liquor 1:7 (f) Pressure kg/cm² 5.0

| Expt. No. | NaOH % | Unbleached yield % | Permanganate number | Breaking length in metre | Tear factor | Burst factor | Brightness % |
|---|---|---|---|---|---|---|---|
| 1. | 4.0 | Remained | undigested | – | – | – | – |
| 2. | 6.0 | 60.00 | 22.54 | 2924 | 73.11 | 49.63 | 25.0 |
| 3. | 8.0 | 58.51 | 15.56 | 3900 | 79.20 | 66.21 | 33.4 |
| 4. | 10.0 | 57.94 | 9.00 | 4656 | 80.03 | 79.03 | 50.1 |
| 5. | 12.0 | 55.12 | 7.42 | 4847 | 80.08 | 84.90 | 56.3 |

Table 2. Effect of sulphur on pulp-yield and permaganate number of the unbleached pulp and physical properties of the unbleached pulp-sheets from soda-sulphur pulp of rice-straw

(a) Material taken in g.o.d. basis 1000 (b) % NaOH 10.0 (c) Temperature °C 150 (d) Time in hours including 50 minutes to reach the temperature 2.5 (e) Material : liquor 1:7 (f) Pressure kg/cm² 5.0

| Expt. No. | Sulphur % | Unbleached yield % | Permanganate number | Breaking length in metre | Tear factor | Burst factor | Brightness % |
|---|---|---|---|---|---|---|---|
| 6. | 0.0 | 49.16 | 10.04 | 3448 | 45.19 | 48.53 | 47.8 |
| 7. | 0.5 | 52.83 | 9.47 | 3825 | 69.78 | 65.76 | 49.3 |
| 8. | 1.0 | 57.94 | 9.00 | 4656 | 80.03 | 79.03 | 50.1 |
| 9. | 1.5 | 58.15 | 9.06 | 4644 | 80.10 | 78.85 | 49.8 |
| 10. | 2.0 | 58.30 | 9.10 | 4633 | 80.22 | 78.67 | 49.0 |

Table 3. Effect of temperature on pulp-yield and permaganate number of the unbleached pulp and physical properties of the unbleached pulp-sheets from soda-sulphur pulp of rice-straw

(a) Material taken in g.o.d. basis 1000 (b) % NaOH 10.0 (c) % Sulphur 1.0 (d) Time in hours including 50 minutes to reach the temperature 2.5 (e) Material : Liquor1:7 (f) Pressure kg/cm$^2$ 5.0 at 150$^o$C

| Expt. No. | Temperature $^o$C | Unbleached yield % | Permanganate number | Breaking length in metre | Tear factor | Burst factor | Brightness % |
|---|---|---|---|---|---|---|---|
| 11. | 140 | 59.63 | 10.52 | 3672 | 76.14 | 68.33 | 43.9 |
| 12. | 150 | 57.94 | 9.00 | 4656 | 80.03 | 79.03 | 50.1 |
| 13. | 160 | 54.31 | 7.46 | 5050 | 73.56 | 86.10 | 55.4 |

Table 4. Effect of time on pulp-yield and permanganate number of the unbleached pulp and physical properties of the unbleached pulp-sheets from soda-sulphur pulp of rice-straw.

(a) Material taken in g.o.d. basis 1000 (b) % NaOH 10.0 (c) % sulphur 1.0 (d) Temperature $^o$C 150 (e) Material : Liquor 1:7 (f) Pressure kg/cm$^2$ 5.0

| Expt. No. | Time in hours | Unbleached yield (%) | Permanganate number | Breaking length in metre | Tear factor | Burst factor | Brightness % |
|---|---|---|---|---|---|---|---|
| 14. | 2.0 | 58.98 | 11.11 | 4407 | 72.16 | 75.92 | 45.0 |
| 15. | 2.5 | 57.94 | 9.00 | 4656 | 80.03 | 79.03 | 50.1 |
| 16. | 3.0 | 54.73 | 7.34 | 4860 | 76.39 | 84.25 | 54.8 |

Table 5. Effect of material-liquor ratio on pulp-yield and permanganate number of the unbleached pulp and physical properties of the unbleached pulp-sheets from soda-sulphur pulp of rice straw.

(a) Material taken in g.o.d. basis 1000 (b) % NaOH 10.0 (c) % Sulphur 1.0 (d) Temperature $^o$C 150 (e) Time in hours including 50 minutes to reach the temperature 2.5 (f) Pressure kg/cm$^2$ 5.0

| Expt. No. | Material liquor ratio | Unbleached yield (%) | Permanganate number | Breaking length in metre | Tear factor | Burst factor | Brightness (%) |
|---|---|---|---|---|---|---|---|
| 17. | 1:6 | 57.75 | 9.24 | 4600 | 79.58 | 78.65 | 48.9 |
| 18. | 1:7 | 57.94 | 9.00 | 4656 | 80.03 | 79.03 | 50.1 |
| 19. | 1:8 | 57.21 | 8.62 | 4705 | 79.34 | 80.55 | 51.2 |

is the formation of sodium hydrosulphide which reduces injurious effects of sodium hydroxide on cellulose and hemicellulose producing higher yields and stronger pulps. Hydrosulphide reacts with lignin producing active thiolignin which reduces time for pulping. Time in case of soda-sulphur pulp of rice-straw was reduced from 3.0 hours to 2.5 hours.

The permaganate number for soda-sulphur pulp was 9.0 which is lower than that obtained by Talwar [10]. The permaganate number showed that the higher pulp-yields were obtained indicating the optimum pulping conditions Table 6 for good delignification.

The brightness for CEH and CEHEH pulps were 78.3% and 80.0% respectively, the later being higher than those

Table 6. Optimum conditions for soda-sulphur cooking of rice-straw.

| NaOH (%) | Sulphur (%) | Tempera-ture oC | Time in hours | Material liquor ratio | Pressure kg/cm$^2$ |
|---|---|---|---|---|---|
| 10 | 1.0 | 150 | 2.5 | 1:7 | 5.0 |

Table 7. Laboratory evaluation of unbleached soda-sulphur pulp of rice-straw.

| Beating time in minutes | Breaking length in metre | Tear factor | Burst factor | Freeness in ml. |
|---|---|---|---|---|
| 00 | 4656 | 80.03 | 79.03 | 910 |
| 10 | 4505 | 83.54 | 76.47 | 902 |
| 20 | 4343 | 92.50 | 73.72 | 891 |
| 30 | 4221 | 97.71 | 71.65 | 882 |
| 40 | 4110 | 110.00 | 69.76 | 871 |
| 50 | 3900 | 126.64 | 66.20 | 863 |
| 60 | 3807 | 119.43 | 64.62 | 855 |

Table 8. Laboratory evaluation of 3-stage CEH bleached soda-sulphur pulp of rice-straw.

| Beating time in minutes | Breaking length in metre | Tear factor | Burst factor | Freeness in ml. |
|---|---|---|---|---|
| 00 | 5563 | 97.81 | 89.93 | 887 |
| 10 | 5417 | 98.07 | 87.57 | 876 |
| 20 | 5285 | 104.38 | 85.44 | 867 |
| 30 | 5150 | 110.00 | 83.25 | 857 |
| 40 | 5020 | 133.87 | 81.45 | 848 |
| 50 | 4903 | 145.54 | 79.04 | 839 |
| 60 | 4787 | 136.13 | 77.39 | 830 |

obtained by previous workers [5,10,11].

Rice straw pulp fibre is short as compared to the fibre-length and fibre-diameter (Table 11) of CEH and CEHEH bleached pulps.

The tear factors of pulps of rice-straw with other bleached pulps at 50 minutes beating time for CEH and CEHEH soda-sulphur pulps were highest being 145.54 and 141.67 respectively (Table 8, 9).

Table 9. Laboratory evaluation of 5-stage CEHEH bleached soda-sulphur pulp of rice-straw.

| Beating time in minutes | Breaking length in metre | Tear factor | Brust factor | Freeness in ml. |
|---|---|---|---|---|
| 00 | 4021 | 86.45 | 62.00 | 876 |
| 10 | 3844 | 90.68 | 59.27 | 866 |
| 20 | 3756 | 95.45 | 57.91 | 854 |
| 30 | 3624 | 104.08 | 55.88 | 843 |
| 40 | 3540 | 123.22 | 54.58 | 832 |
| 50 | 3406 | 141.67 | 52.52 | 822 |
| 60 | 3368 | 136.75 | 51.03 | 811 |

Table 10. Yield and brightness of the bleached soda-sulphur pulp of rice-straw.

| Type of bleached pulp | Bleached yield (%) | Brightness (%) |
|---|---|---|
| CEH | 51.00 | 78.3 |
| CEHEH | 49.05 | 80.0 |

Table 11. Fibre-dminsions of soda-sulphur pulp of rice-straw.

| Type of bleached pulp | Length in mm | | | Diameter in mm | | |
|---|---|---|---|---|---|---|
| | Maxi-mum | Mini-mum | Aver-age | Maxi-mum | Mini-mum | Aver-age |
| CEH | 1.88 | 0.56 | 1.08 | 0.0098 | 0.0033 | 0.0066 |
| CEHEH | 1.80 | 0.52 | 1.06 | 0.0098 | 0.0033 | 0.0066 |

Table 12. Fibre-fraction of soda-sulphur pulp of rice-straw.

| Type of bleached pulp | 0.50 – 0.99 (mm) | 1.00 – 1.49 (mm) | 1.50 – 1.99 (mm) | 2.00 – 2.49 (mm) | 2.50 – 2.99 (mm) | 3.00 – 3.49 (mm) | 3.50 – 3.99 (mm) | 4.00 – 4.49 (mm) |
|---|---|---|---|---|---|---|---|---|
| CEH | 46.15 | 36.85 | 18.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CEHEH | 37.87 | 54.00 | 8.13 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |

## CONCLUSION

Writing good quality newsprint, wrapping, packing and printing paper can be made from CEH and CEHEH soda-sulphur pulp of rice-straw. Papers may be easily made from laboratory evaluated unbleached one.

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