Alkaline Pulping of Straws with Anthraquinone

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ABSTRACT

Alkaline pulping of wheat straw and rice straw was carried out under varying conditions of alkali concentration, time and temperature. Effect of sulphidity and anthraquinone (AQ) addition was examined. It was found that the advantages of AQ addition in pulping were evident even in atmospheric pressure pulping. Easily bleached pulps in about 50-52% yield and of 70% brightness could be prepared.

Cereal straws, particularly of rice and wheat are abundantly available in our country and could easily supplement the growing requirements of paper pulps provided their pulping is made more efficient and economical than at present. Considerable work has been reported on modification of the existing processes to achieve this goal [1–7] Apart from conservation of energy and resources the need to abate air and water pollution is another constraint on the development of new processes.

Anthraquinone (AQ) as an additive in pulping appears promising to meet many of such requirements. It gives a dramatic increase in yield, reduces chemical consumption thereby making the process more economical and helps to avoid the use of sulphur chemicals which emit obnoxious gases and are scarcely available in our country. Since Holton's discovery of its use, a large number of papers have appeared reporting the advantages of its addition in pulping[8–21].

The chemical mechanism of alkaline AQ pulping is fairly well known with AQ being described as a redox catalyst (See Fig.1 and 2). The reactions of lignin units with hydroxyl ion, hydrosulphide ion and with Anthrahydroquinone (AHQ), the reduced form of AQ, have been schematically shown in Fig. 1 and 3. The AQ while being reduced to AHQ, oxidises the reducing end group of cellulose and hemicelluloses, thus preventing the peeling reaction in alkali and enhances the pulp yield. AQ is regenerated from AHQ by reaction with lignin[5], 22–24 (Fig.3).

The present work describes the effect of addition of anthraquinone in alkaline pulping of straws with boiling at atmospheric pressure and a comparison of the results with the conventional methods of pulping.

Results and Discussion :

The analysis of wheat and rice straw shows that these materials are rich in hemicelluloses as indicated by the high pentosans content. The alpha cellulose content is only 26% in rice and 32% in wheat straw (See Table 1). The straw grows to its full height in barely 3 months and so have a less developed and open morphological structure. It should be possible to delignify them with mild treatments using lesser chemicals and heat energy as compared to wood and bamboo[2].

Results of pulping of wheat straw with alkali at 140°C have been given in Table 2 (1 to 6). The effect of increase in alkali concentration has also been shown in Fig. 1. It was found that the pulp yield is maximum (54.0%) for a low kappa number (22.6) when 12% alkali on straw is used. A similar series of experiments on rice straw (Table 3 and Fig. 1) have shown that 10 % alkali is sufficient to give a yield of 53.5% at a K. Number of 18.9. These concentrations of alkali were used for subsequent runs with the addition of sodium sulphide or A.Q.

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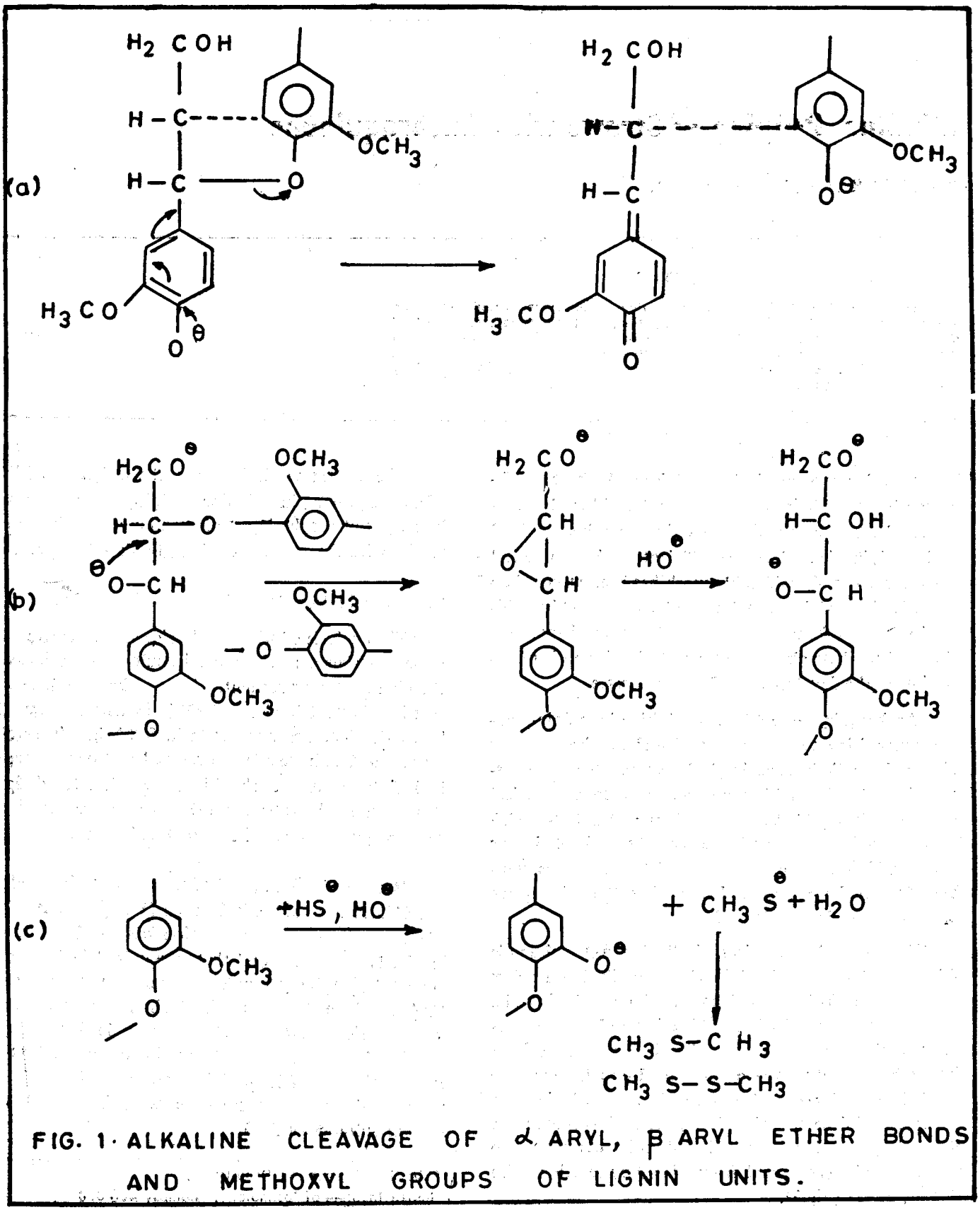


FIG. 1 · ALKALINE CLEAVAGE OF α ARYL, β ARYL ETHER BONDS AND METHOXYL GROUPS OF LIGNIN UNITS.

FIG—1

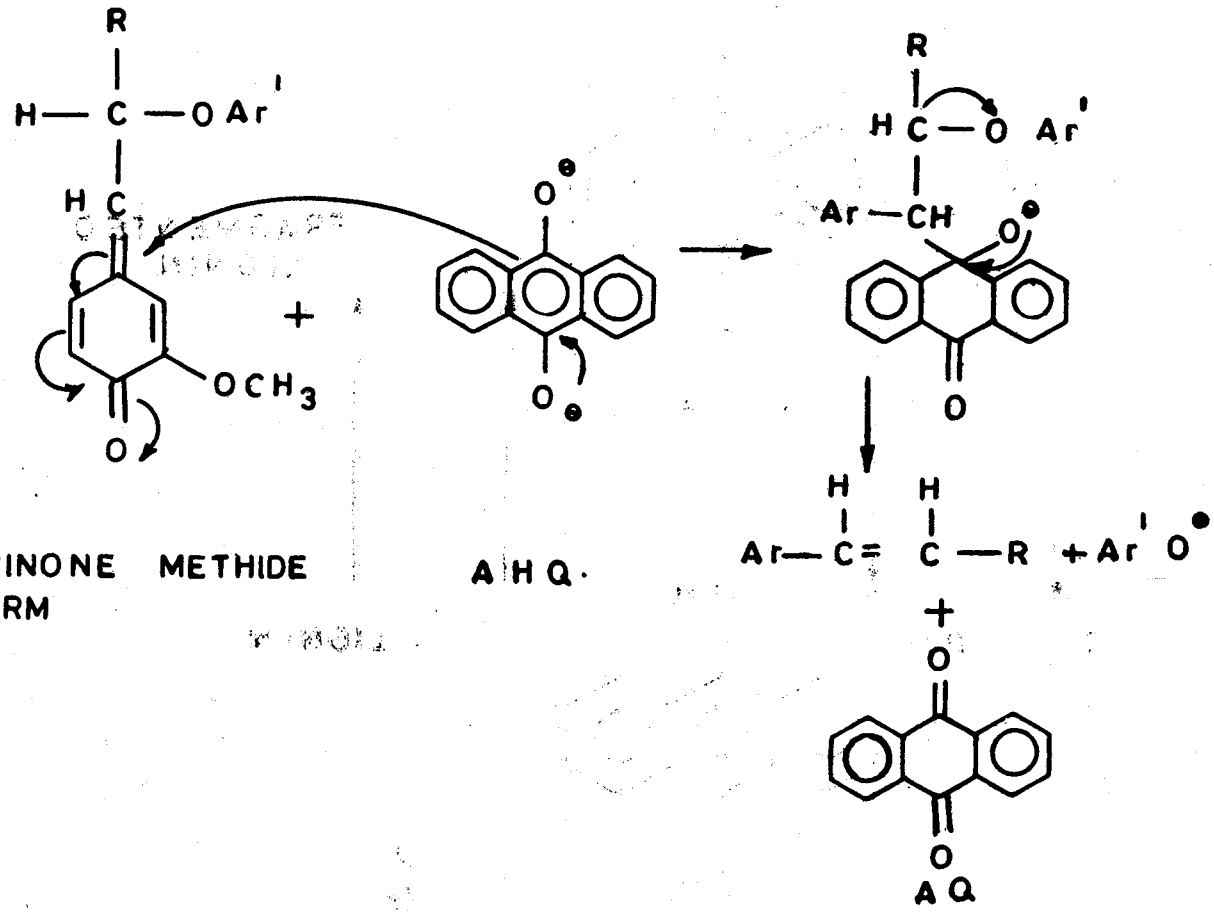


FIG. 3: REACTION OF ANTHRAHYDROQUINONE WITH PHENOLIC ARYL PROPANE UNITS.

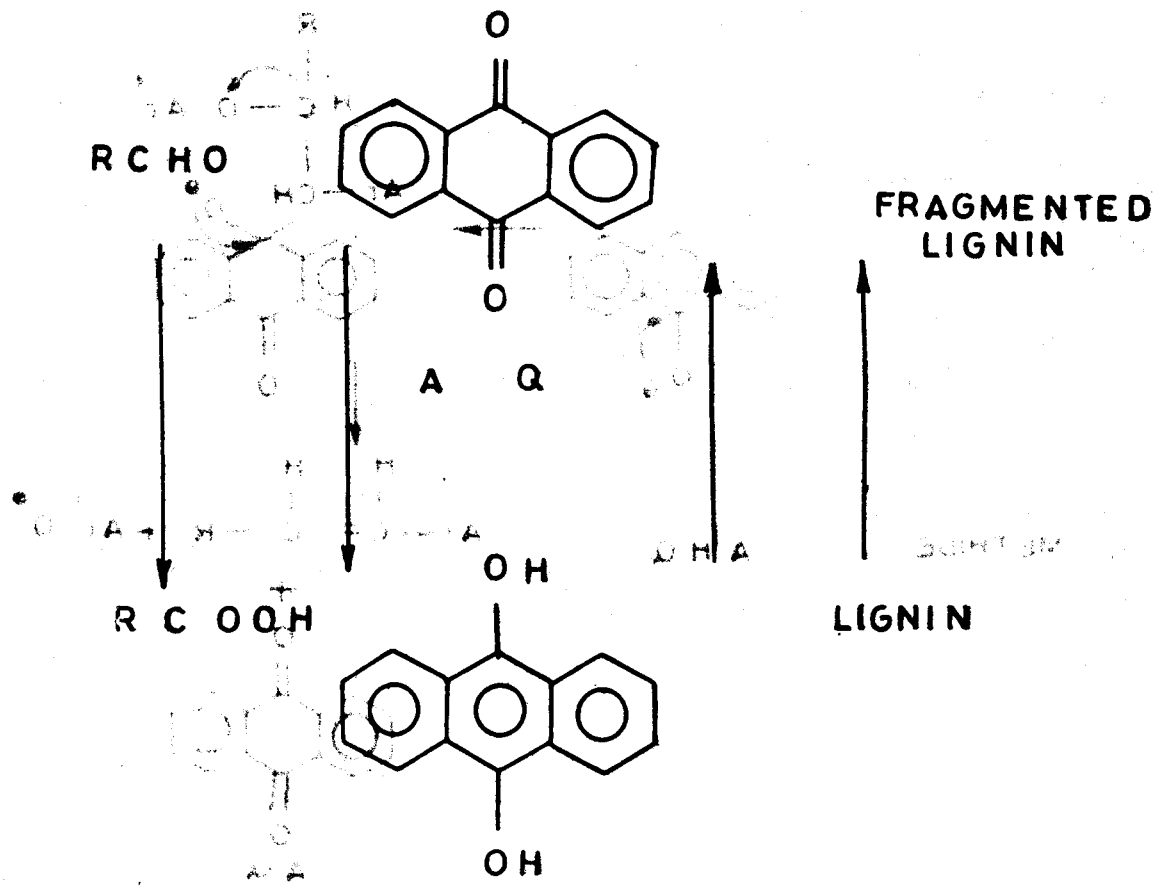


FIG. 2: REDOX CYCLE AND ACTION OF ANTHRAQUINONE.

Use of cooking liquor with 12 and 10% active alkali and 12% sulphidity, both for wheat straw and rice straw have been found to have a very marginal effect on yield and K Number of wheat straw, though in case of rice straw the K Number decreased by 1.9 [See run No. 6 of Table 2 and 3]. It shows that the wheat straw lignin is devoid of groups which respond to additional delignification by HS^- ion[35]. A similar effect of sulphidity was noted at ambient pressure pulping of wheat and rice straw (Run 14, 15 of Table 2 and 3). A notable feature is that the sulphidity does not show even the slight improvement in K. Number of rice straw under these conditions, as was noticed in pressure pulping. It corroborates our view that the sulphidity does not offer any additional advantage in pulping of straws.

The effect of addition of AQ on pulping of wheat straw with 12% alkali can be seen from Table 2 and Fig. 5. The AQ addition results in an increase in yield and simultaneous decrease in K. Number. The maximum effect is observed with an AQ addition of 0.05% on straw. An increase in quantity of AQ does not give corresponding advantage in yield and K. Number. In fact the effect tapers off to a constant increase in yield and decrease in K. Number after 0.1% AQ. At 0.05% addition the yield increase is observed to be 1.6 and decrease in K. Number by 1.2 points.

Table—1

SUMMATIVE ANALYSIS OF STRAWS

(Percent based on even dry straw)

Constituents	Rice straw	Wheat straw
Ash	14.4	8.0
Hot water solubles	18.0	9.9
Alcohol benzene solubles	1.7	5.5
Pentosans	21.1	23.5
Lignin	19.9	21.5
Alpha cellulose	25.9	32.2

Table — 2

PULPING OF WHEAT STRAW

S. No.	Active alkali as Na_2O%	A Q added % of o.d. straw	Pulp yield %	Kappa Number
1	6	Nil	65.0	31.0
2	8	,,	60.5	27.2
3	10	,,	56.5	23.8
4	12	,,	54.0	22.6
5	14	,,	52.3	21.6
*6	12	,,	54.5	22.4
7	12	.02	54.7	21.5
8	12	.05	55.6	20.4
9	12	.10	56.0	20 0
10	12	.15	56.2	19 9
11	12	Nil	59.2	22.3
12	12	.05	60.0	18.9
13	12	.10	60.2	18.0
*14	14	Nil	58.2	20.2
15	14	Nil	58.0	20.4

Pulping conditions: (For 1 to 10) — Bath ratio 1:5,
Temperature 30 to 140°C — 30 min, at 140°C — 120 min,
(For 11 to 15) — Bath ratio 1:20, Temperature 90 min at boil.

* For 6 and 14, sulphidity of 12 % was kept.

Table — 3

PULPING OF RICE STRAW

S. No.	Active alkali as Na_2O %	A. Q. added % of o.d. straw	Pulp yield %	Kappa Number
1	6	Nil	63.0	30.0
2	8	,,	56.8	23.6
3	10	,,	53.5	18.9
4	12	,,	51.0	18.0
5	14	,,	48.5	17.5
*6	10	,,	53.8	17.0
7	10	.02	54.0	17.4
8	10	.05	54.6	15.7
9	10	.10	55.1	15.2
10	10	.15	55.2	15.0
11	10	Nil	53.5	17.8
12	10	.05	54.1	15.0
13	10	.10	54.5	15.0
*14	12	Nil	51.2	18.1
15	12	,,	50.0	18.2

Pulping conditions : (For 1 to 10)—Bath ratio 1:6, Temperature 30 to 140°C—30 min, at 140°C—120 min.
(For 11 to 15) — Bath ratio 1:20, Temperature.
*For 6 and 14, sulphidity of 12% was kept.

Table — 4

BLEACHING OF STRAW PULPS

		Wheat straw			Rice straw		
		4	8	12	3	8	13
1.	Kappa Number	22.6	20.4	18.9	18.9	15.7	15.0
2.	Chlorine demand %	9.2	8.5	7.9	8.0	7.5	7.2
3.	Chlorine added in Hypo I	7.4	6.8	6.3	6.4	6.0	5.7
4.	Alkali added	1.2	1.2	1.2	1.0	1.0	1.0
5.	Chlorine added in Hypo II	1.8	1.7	1.6	1.6	1.5	1.5
6.	Bleached pulp yield on o.d. straw	52.0	52.5	52.5	49.6	51.4	51.0
7.	Brightness %	71.0	71.2	72.2	70.0	68.0	71.5

Constant conditions — consistency — 5 %, temperature 40 °C, time 90 min, pH—9.5 to 10
Alkali extraction for 60 min at 70 °C.

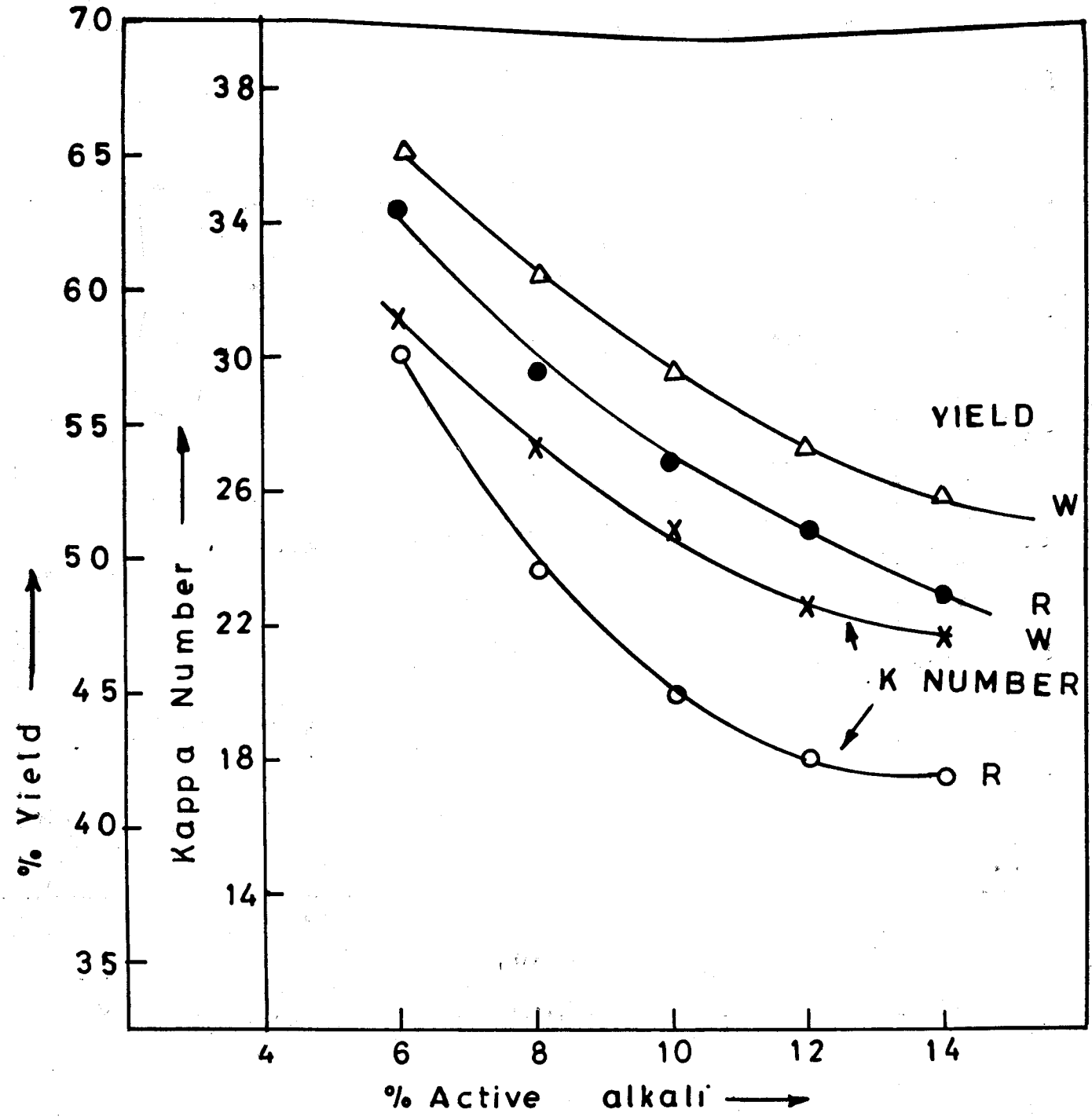
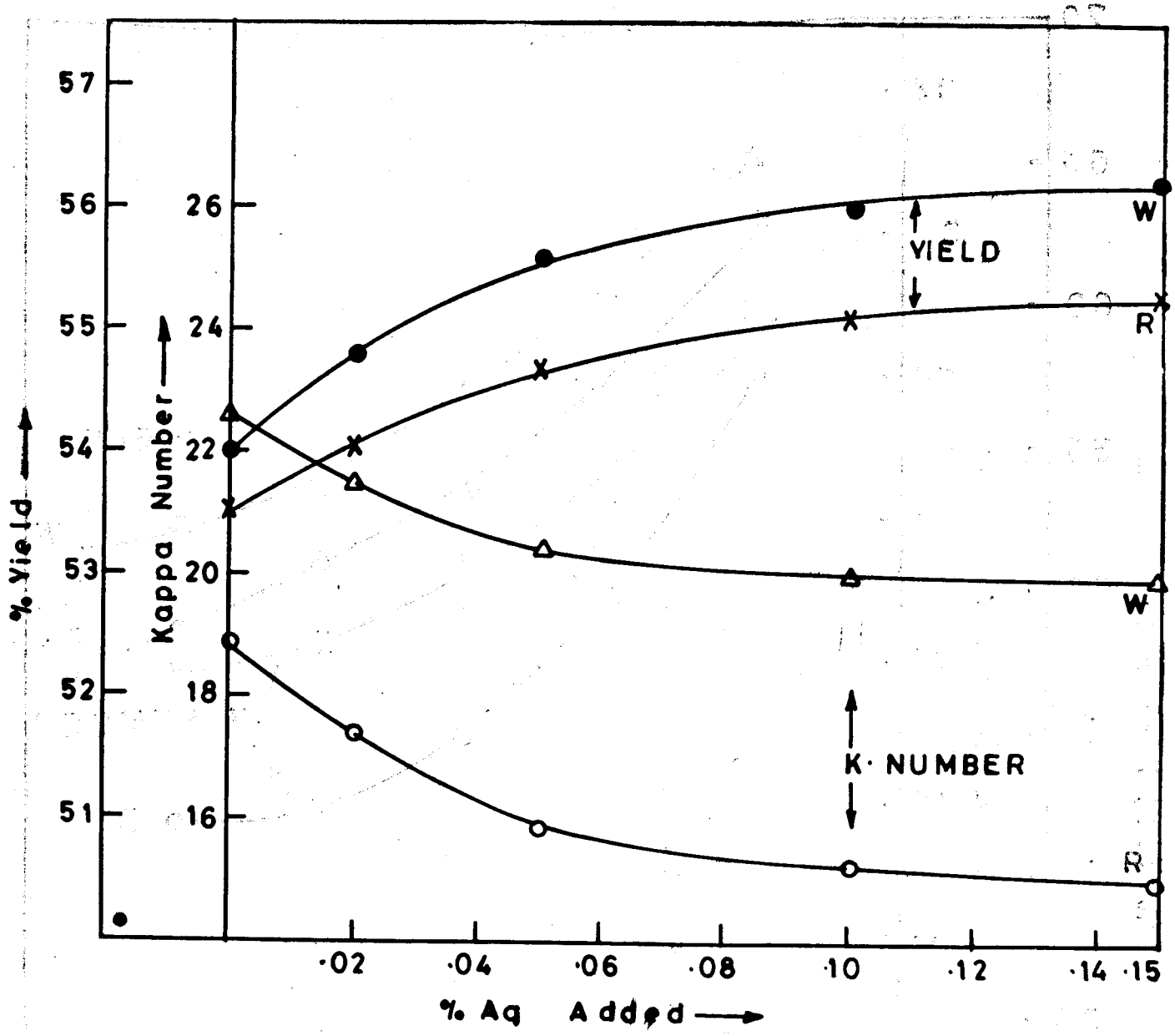


FIG. 4 : EFFECT OF % ALKALI ON YIELD AND KAPPA NUMBER OF STRAWS.



FIG·5: EFFECT OF AQ· ADDITION ON PULPING.

A similar effect was noticed when rice straw was cooked with 10% alkali and AQ. (Table 3 and Fig. 5). The increase in yield was found to be 1.1 and the decrease in K Number by 3.2 points when 0.05% AQ on straw was added- The fact that the yield increase is observed due to retention of Arabinoxylans from hemicelluloses of straws, has been pointed out by earlier workers[17-26]. It is also evident that the delignification of straws is enhanced by AQ addition as shown by a decrease in K. Number.

The success of AQ addition in alkaline pressure pulping of straws prompted us to try its effect on ambient pressure pulping of straws. The conditions for maximum delignification of straws with alkali boil at ambient pressures has been established earlier in this laboratory[1,2,7]. When these cooks were performed with AQ addition (12,13 in Table 2 and 3), it was found that the same effects, that is an increase in yield and decrease in K Number were noticeable, the later being more pronounced. There was a marginal increase of 0.8 and 0.6 in yield of wheat and rice straw respectively, whereas a substantial decrease of K. Number by 3.4 and 2.8 points was observed when 0.05% AQ was added both on wheat and rice straw.

These results have pointed out that the enhanced delignification of straws due to AQ addition can be realised at much lower temperatures (about100 °C) than those normally used for pulping. A correspondingly lesser rise in yield as compared to pressure pulping, is probably due to the fact that the degradation of carbohydrates and its prevention by AQ addition is more prominent, at higher temperatures in pulping.

Bleaching experiments with these pulps obtained with and without AQ addition showed the trends as given in (Table 4).

Chlorine demand of wheat straw pulps was found to be about 41% of the Kappa Number whereas it was around 46% of K. Number for rice straw pulps.

Two stage hypochlorite treatment with an intermediate alkali extraction stage was sufficient to obtain pulps of brightness of about 70% from unbleached pulps of straws. The advantage of yield gained during AQ pulping was retained even after bleaching and it can be said that AQ addition gives pulps of comparable yield and brightness to those obtained in alkali pulping, with an advatage of reduced consumption of bleaching chemicals.

Conclusions

1. An AQ addition of 0.05% on straws is sufficient to derive maximum benefits of an increased yield and decreased Kappa Number in alkali pulping of wheat and rice straw.
2. Advantages of AQ addition are obtained even in alkali boiling of straws at ambient pressures which give pulps of comparable yield and K. Number.
3. Characteristics of bleached pulps such as yield and brightness remain unaffected by AQ addition during pulping.

Experimental

Wheat straw and Rice straw available from a local board mill were cut to small pieces (15—20mm) and stored over sodium chloride solution. A moisture content of 13% was maintained. Samples were drawn from this stock. Anthraquinone. sodium hydroxide and other chemicals used were chemically pure grade.

A one litre digester immersed in a glycerine bath with temperature control was used for the pressure pulping. Alkali was used for the pressure pulping. Alkali boil was performed in steel equipments.

About 100 g of straw exactly weighed was used for each run and the average results of several consistent runs have been given in the tables. For a few runs a sulphidity of 12% was maintained in the cooking liquor. Bleaching by sodium hypochlorite was done in two stages using glass equipment and constant temperatare baths.

Tappi methods were used for all analyses

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Literature cited :

1. Kamath, N.R. and Sindhanty, A.R., *Ind. Pulp Paper, 23* 265 (1968).
2. Trivedi, M.K., *Ippta, 18,* 1 (1980).

3. Casey, J. P., Pulp and Paper-chemistry and chemical technology, John Wiley, New York, 3rd ed. 1980, Vol. I, pp. 70-140.

4. Vardhan, R., Swamy, V.S.R., Murthy, N.Y.S.R. and Rao, A.R.K., *Ippta* 11 (4), 257 (1974).

5. Fengel, D. and Wegener, G., Wood-chemistry, Ultrastructure, reactions, Walter de Gruyter, New York, 1984.

6. Jene, S.C., Rao, Y.S., Maheswari, S. and Bihani, B.L., *Ippta 22*, (3), 35 (1985).

7. Trivedi, M.K., *Ippta 12*, 308 (1975).

8. Holton, H.H., *Pulp Paper Canada, 78* (10), T 218 (1977).

9. Holton, H H., *Svensk Papperstidn, 84* (10) 37 (1981).

10. Farrington, A , Nelson, P.F. and Vanderhock, N., *Appita, 21* (2), 119 (1977).

11. Holton, H.H. and Chapman, F.L , *Tappi, 60* 11 121 (1977).

12. Madan, R.N., *Ippta 16* (3) 117 (1979).

13. Chowdhary, L.N., Saksena, U.L., Subhash Chandra and Singh B , *Ibid*, 143 (1979).

14. Rawat, R., Sharma, G.D., Bhargawa, G. G. and Singh, M.M., *Ippta 22* (3), 39 (1985).

15. Nayak, R.G., Handigol, S.G., Meshramkar, P.M., Deb, U. K. and Jaspal, N. S., Ippta *17* (1) 31 (1980).

16. Jauhari, M.B. and Ghosh, P.C., *Ippta*, 21 (1) 45 (1984).

17. Sood, Y.V. and Kapoor, S.K., *Ibid*, 81 (1984).

18. Goyal, P. and Mishra, N. D., *Ippta 19* (1), 1 (1982).

19. Shah. S.J., Abhyankar, S.H, Rao, T G., Nagarkar, A.P. and Sadawarte, N.S., *Ibid*, 6 (1982).

20. Sharma, Y. K. and Bhandari, K.S., *Ibid*, 12 (1982).

21. Holton, H.H. and Kutney, G.W., *Chemtech*, Sept. 1985, P, 568.

22. Flemimg, B I., Kubes, G. J., Macleod, J. M. and Bolkar, H.I., *Tappi 61* (6) 43 (1978).

23. Lowendahl, L. and Samuelson, O., *Tappi 61* (2), 19 (1978).

24. Gierer, J. and Noren, I., *Halzforshung 34*, 197 (1980).

25. Gierer, J. and Ljunggren, S., *Svensk Papperstidn, 82*, 503 (1979).

26. Matter, S.M. and Fleming, B.I., *Tappi, 64* (4) 136 (1981).

27. Sinha, K.P., Pande, G.C. and Seth, A. P , *Ippta*, 20 (3) 57 (1983).