2015 International Conference on Advances in Environment Research
Volume 87 of IPCBEE (2015)
DOI: 10.7763/IPCBEE. 2015. V87. 8

Caustic Soda Delignification of Khar Grass for Separation of Cellulosic Fibers

Akhouri Sanjay Kumar Sinha [1 +]

[1] Department of Chemical Engineering, Sant Longowal Institute of Engineering & Technology, Longowal-148106, Punjab, India

Abstract. Scarcity of forest based woody raw materials is forcing for research and development in the area of non woody raw materials like agricultural residues and grasses available in abundant quantity. Experimental analysis shows that Khar grass contains 21 percent lignin, 79 percent holocellulose, 27 percent pentosans and 5 percent ash. Soda pulping process with different NaOH percentage was used for delignification. Pulp obtained was analyzed by fiber classification, coarseness and photomicrography. The fiber length varies between 0.88 to 1.00 mm. The paper made of khar grass pulp can have tensile index 80 – 90, burst index 4.5 – 5.0 Kpa/gsm and folding endurance of 1.4 to 1.5. These strength properties are quite enough for manufacturing average grades of writing and printing papers.

Keywords: Delignification, caustic soda, cellulosic fibres, lignin

1. Introduction

The pulp and paper industry is a core sector having important role to play in the development of society at the global level. The usage of paper is considered as an indexing symbol of cultural growth. There are more than 600 pulp and paper mills in India producing a range of paper varieties. Nearly 6.2 million tons of paper and paperboard is produced in India. Nearly 64% of the paper production comes from the non-forest based raw materials and termed as non-conventional raw materials such as agro residues and waste paper [1]. The pulp & paper industry is facing tough challenges in form of scarcity of fibrous raw materials more strict environmental rules and regulations, less energy usage and lower profit margins for common grades of paper. There are 759 paper mills in India with an annual capacity of 12.7 million tonnes and consumption at 11 million tonnes. The per capita paper consumption is 9.3 kg per year. The projected demand for paper by 2025 is 24 million tones leading to a shortfall of 12 million tones of wood [2]. Therefore, new or modified raw materials and suitable technology is required. Now a days there is huge crisis of wooden trees especially in developing countries, thus to overcome this problem non woody raw materials like khar grass need to be explored and used. Main basic material for paper making is cellulose fibers, which usually consists of over 500,000 cellulose molecules. SaccharumMunja, known as munja also is found in arid areas and along river banks in India. It belongs to the family Gramineae. It is commonly called as Sarkanda is available in large quantity in north India. It is 2-2.5 meters long and have diameter in the range of 1 to 1.5 cm for a fully grown plant. Hollucellulose, klason lignin, pentosans and ash percentage in SaccharumMunja are 79.13, 22.03, 26.5 and 4.67 respectively [3].The use of short fibers along with small percentage of long fibres (obtained from rice straw) provides good strength. Again the use of 15-25 % fillers results in good surface and optical properties [4]-[7]. The earlier study of bleaching processes and effect on silica content in rice straw pulp obtained by catalyzed acetic acid pulping have been studied. This study again highlighted the environment friendly process for processing of rice straw for fibres [8].

+ Corresponding author. Tel.: +1672253698.
E-mail address: akhouri_sanjay@yahoo.com.

2. Experimental

2.1. Material

Khar grass was procured from agricultural fields of Sangrur (Punjab). This was washed with water, air dried, cut into 1cm – 1.1cm long pieces, and packed in air tight plastic containers for subsequent analysis and processing. The proximate analysis of the khar grass was carried out using appropriate TAPPI (Technical Association of Pulp & Paper Industries) methods.

Proximate analysis of khar grass is given below in Table I for most of the important parameters used in industry and research related to paper industry.

Table I: Proximate analysis of khar grass

S.NO.	Analysis	Avg. ± stand. Dev.	TAPPI Method
1.	1% NaOH Solubility [%]	25.7 ±2.8	T-212
2.	Ash [%]	5.0 ±0.3	T-211
3.	Silica [%]	4.3 ± 0.46	T-211
4.	Alcohol benzene solubility [%]	10.75 ±1.42	T-204
5.	Klason lignin [%]	21.0 ± 0.85	T-222
6.	Holocellulose [%]	79.0 ± 2.63	T-203
7.	Pentosans [%]	27.0 ±0.45	T-223
7.	Hot water solubility [%]	11.29 ± 0.45	T-207
8.	Cold water solubility [%]	7.85 ± 0.41	T-207
9.	Moisture content [%]	10.80 ± 0.65	T-210
10.	Bulk density [Kg/m^3]	123.5 ± 1.8	T –258

2.2. Delignification of Khar Grass with Caustic Soda

Delignification (pulping) of khar grass was carried out with caustic soda as the main chemical and H_2SO_4 as a catalyst. The pulping experiments were conducted at various conditions for observation of their effects.

Process variables in pulping are as given below in Table II.

Table II: Process variables in pulping

S. No.	Variable	Values
1	Caustic soda concentration (%)	10, 12, 14, and 16
2	Anthraquinon concentration (%)	0.5, 1.0, 1.5, and 2
3	Time of reaction, min	120, 150, 180, 210
4	Liquor to straw ratio	8, 10, 12 and 14
5	Temperature, ^{0}C	145, 160, 175, and 190

For each experiment, the reaction was carried out for 100 g of oven dry khar grass in polyethylene bags at controlled temperature water bath. After the reaction for a specified time, the residual mass was cooled to 45-50 ^{0}C and filtered out.

2.3. Analysis of the Pulp

The pulps obtained after caustic soda delignification were analyzed for percentage yield, kappa number, holocellulose, klason lignin, ash, and silica content. Selected pulps were also classified in a Bauer Macnett fiber classifier.

2.4. Physical Properties of the Sample Hand Sheet Paper Made from Pulp

Standard handsheets of 100 g/m^2 were prepared in a lab sheet former from the pulps after beating them to 40 ^{0}SR in a lab valley beater. The handsheets were pressed in the lab sheet press and air dried for 24 hrs. The air dried sheets were kept in airtight black polythene bags for subsequent use and analysis of important properties. The handsheets were conditioned for 3 hours in an environment chamber maintained at temperature of 25 ^{0}C and relative humidity of 52 %. The conditioned sheets were tested for brightness,

printing opacity, burst strength, (T 403), tear strength (T 414) and tensile strength (T 494) as per standard TAPPI procedures.

Bleaching conditions for First and Second H (Sodium hypochlorite) stage bleaching are mentioned below in Table III with all the important parameters of reaction.

Table III: Bleaching conditions for First and Second H (Sodium hypochlorite) stage bleaching

Bleaching conditions for First H stage bleaching	Bleaching conditions for Second H stage bleaching:-
Weight of OD pulp taken = 120 gms	Weight of OD pulp taken = 114 gms
NaOCl used = 5% of OD pulp	NaOCl used = 3% of OD pulp
NaOH = 0.5% of OD pulp	NaOH = 0.3% of OD pulp
Time =120 min	Time =120 min
Temp. = 50 ^{o}C	Temp. = 50 ^{o}C
pH = 10	pH = 10
Consistency = 9%	Consistency = 9%

Bleaching conditions for P (hydrogen peroxide) stage and Q (chelating agent) stage bleaching are mentioned below in Table IV with all the reaction parameters.

Table IV: Bleaching conditions for P stage and Q stage bleaching

Standard conditions for H_2O_2, P stage bleaching	Standard conditions for chelating agent, Q stage:-
Weight of OD pulp taken = 105 gms	Weight of OD pulp taken = 100 gms
H_2O_2 used = 5 % of OD pulp	Chelating agent used = EDTA
$MgSO_4$ used = 0.3 % of OD pulp	EDTA used = 0.3 % of OD pulp
NaOH used = 2.5 % OD pulp	Volume of EDTA = 30ml
Time =90 min	Time = 120min.
Temp. = 50 ^{o}C	Temp. = 50 ^{o}C
pH =10	pH = 6-6.5
Consistency = 9%	Consistency = 9 %

3. Results & Discussion

3.1. Chemical Analysis of Raw Material

The alcohol benzene soluble content of SaccharumMunja is a measure of the waxes, fats, resins and certain other ether in soluble components including possible portions of some of the so- called wood gums and other water soluble components.Ash content of SaccharumMunja pulp is defined as the residue remaining after ignition at 575 ^{0}C for 3 hrs or longer if necessary to burn off all carbon. It is a measure of mineral salts and inorganic foreign matter in pulp. Lignin is called the 'incrusting material forming a part of cell wall and middle lamella in SaccharumMunja. It is an aromatic amorphous substance containing methoxyl, hydroxyl and other constituents groups. Fibrous raw materials contains from about 15 to 30% lignin, removal of which is a main objectives of pulping and bleaching processes. The cold water procedure removed a part of extraneous components, such as inorganic compounds, tannins, gums, sugars, and coloring matter present in SaccharumMunja. The hot water procedure removed the starchin addition.

SaccharumMunja contained the non cellulosic carbohydrates called hemicelluloses. Pentosan content of SaccharumMunja showed the quantity of hemicelluloses present in raw material and its pulp. The hemicelluloses were degraded during pulping and bleaching processes.

3.2. Effect of Concentration of Caustic Soda

The increase in concentration of caustic soda improves the delignification and provides better quality pulp with lower lignin content. Pulp yield decreases with increase of caustic soda concentration in liquor due to increase of delignification and solubilization of hemicelluloses in caustic soda. But the quality of pulp obtained at higher pulp yield is not suitable for further processing in paper industry due to high kappa number and residual lignin in pulp. A pulp kappa number equal to 26.2 was obtained at 85 % Acetic acid concentration with 1% catalyst concentration at 90 ^{0}C temperature and 180 minutes of reaction time when liquor to straw ratio was maintained at 10. The detailed effects are shown in graphs given in Fig. 1.

3.3. Effect of Catalyst Concentration

Anthraquinon concentration of 1% provides the best delignification, minimum kappa number and maximum holocellulose percentage in pulp with minimum Residual lignin. The detailed effects are shown in graphs given in Fig. 2.

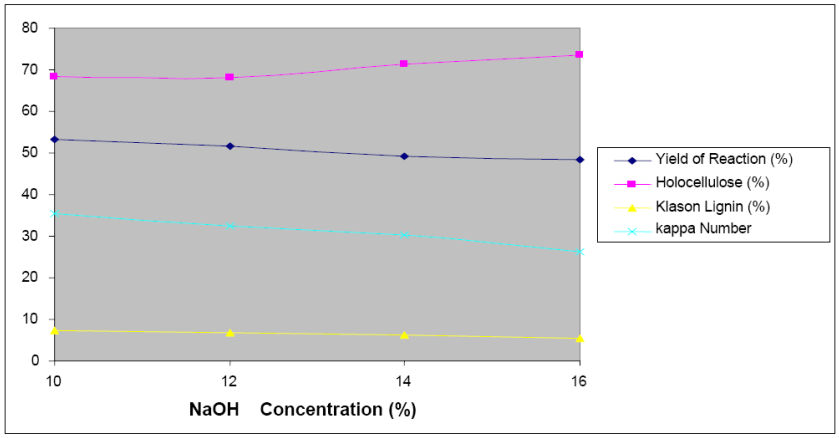

Fig. 1: Effect of Caustic soda concentration on pulp Yield, holocellulose, klason lignin and Kappa Number

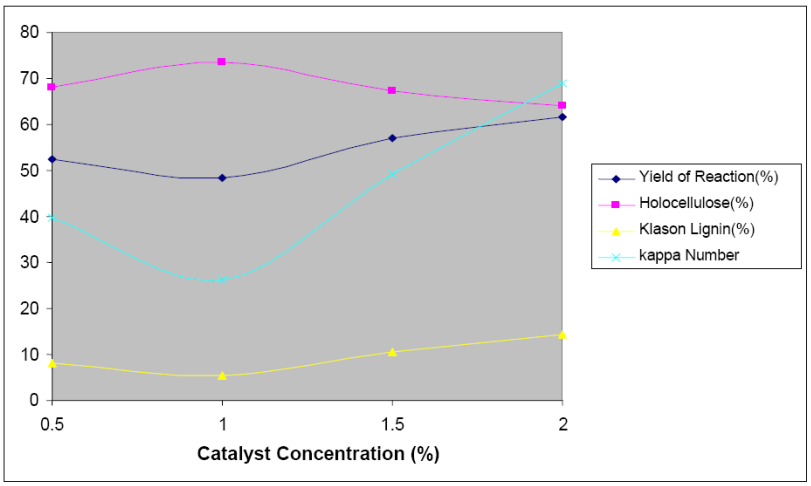

Fig. 2: Effect of catalyst concentration on pulp Yield, holocellulose, klason lignin and Kappa Number

3.4. Effect of LSR (Liquor to Straw Ratio)

The amount of liquor to straw is an important parameter for uniform and efficient delignification reaction. The whole mass of khar grass (solid phase) should be in contact of another reactant caustic soda which is present in liquid phase. Again the catalyst is in liquid phase only. The LSR was varied from 8 to 14 and best result was obtained at a LSR equal to 10. The detailed effects are shown in graphs given in Fig. 3.

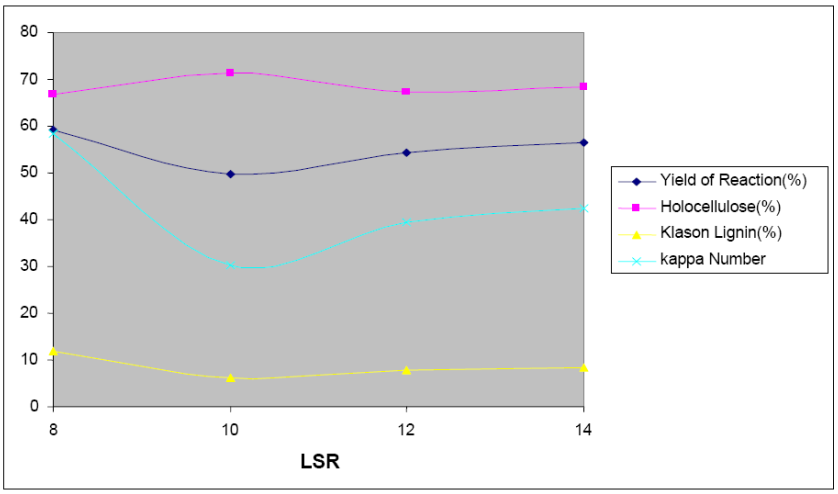

Fig. 3: Effect of LSR (Liquor to Straw Ratio) on pulp Yield, holocellulose, klason lignin and Kappa Number.

3.5. Effect of Temperature

The increase of temperature of reaction from 145 ^{0}C to 190 ^{0}C has shown the decrease of Klason lignin percentage by slightly more than 50 percent. This is again supported by decrease of kappa number of pulp from nearly 65 to 26. The constituents of raw material get degraded in reaction, the overall yield decreases significantly. The detailed effects are shown in graphs given in Fig. 4.

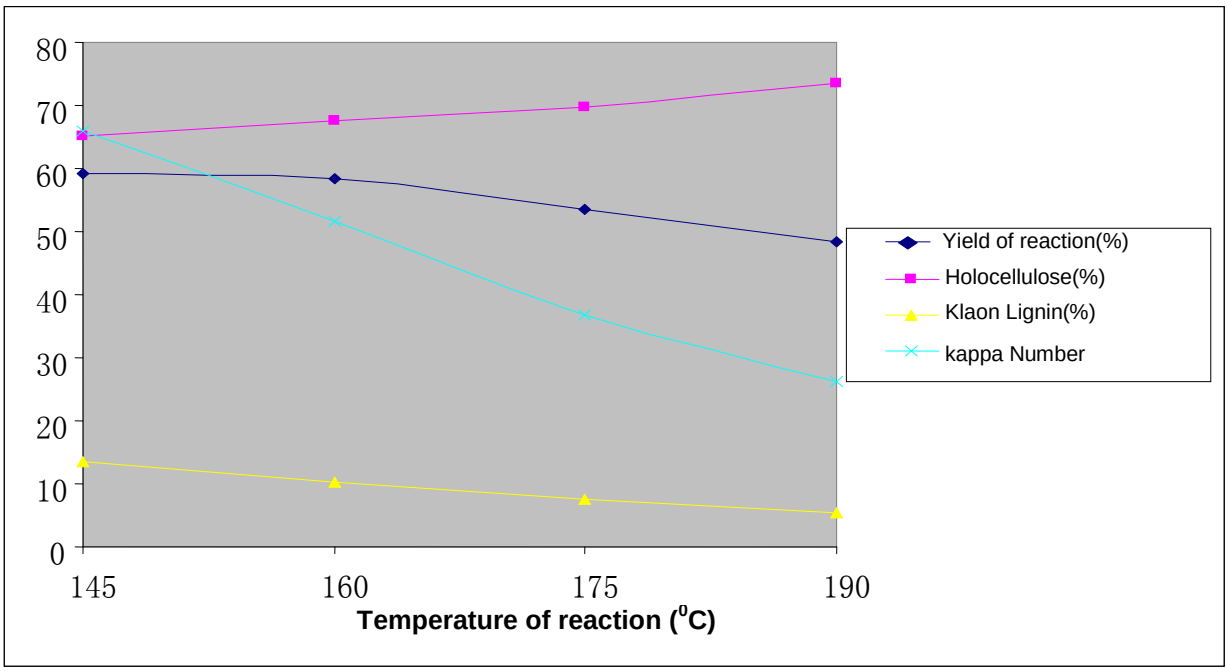

Fig. 4: Effect of temperature of reaction on yield, holocellulose, klason lignin and kappa number

3.6. Effect Reaction Time

Reaction time increase leads to completion of reaction. Time increase up to 180 minutes results in lowering of lignin percentage in pulp to a level of 5.7 percent from 21 percent which shows a significant change. Further increase of time does not help in delignification. The change of kappa number also shows the similar trends. Detailed effects of time variation are shown in graphs given in Fig. 5.

3.7. Analysis of Pulp Obtained after Reaction by Caustic Soda

The important chemical composition factors affecting the pulp properties for paper making are mentioned below. This shows higher ash content but optimum holocellulose and kappa number.

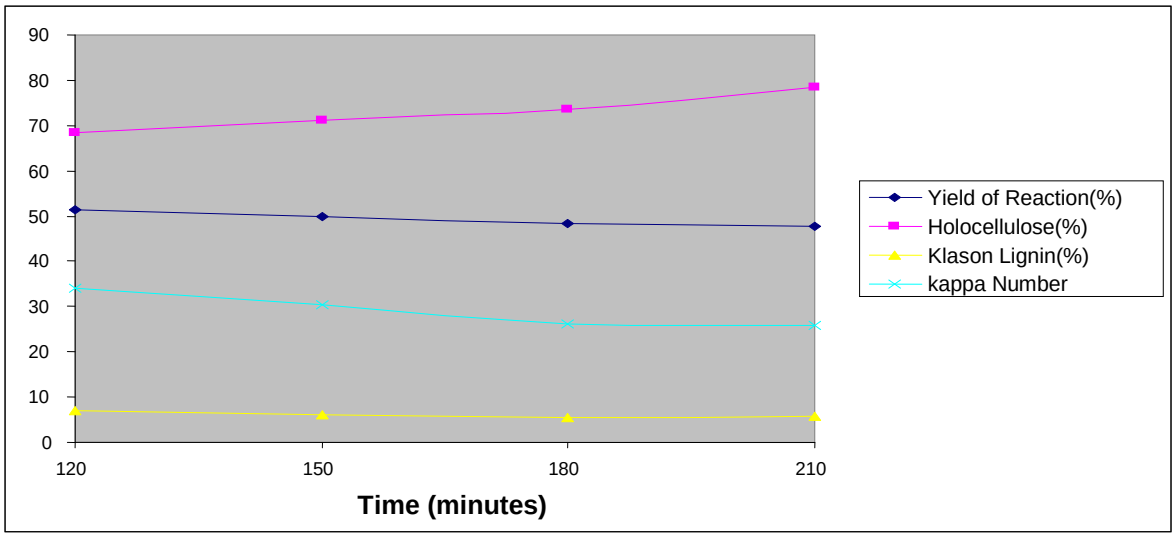

Fig. 5: Effect of time of reaction on yield, holocellulose, klason lignin and kappa number

Chemical composition of khar grass pulp: The important chemical composition factors affecting the pulp properties for paper making are mentioned below in Table V. This shows higher ash content but optimum holocellulose and kappa number.

Table V: Chemical composition of khar grass pulp

Composition	Sachramunj
Ash %	16
Kappa no.	25.32
Silica	8
Solubility a)Hot water b)1% NaOH	 16 40
Alpha cellulose	32
Hollocellulose	52

Paper Properties from khar grass Pulp: The important strength properties and brightness are good for obtained pulp as shown below in Table VI.

Table VI: Paper Properties

Raw Material	Tear Strength (mNm^2/gm)	Burst Strength (Kg/m^2)	Smoothness (sec/100ml air pass)	Brightness (% ISO)
Khar Grass	4.5	0.26	52.65	60.24

Bleaching Results of khar grass Pulp: increase of brightness of pulp with each step of bleaching is shown below in Table VII.

Table VII: Brightness of pulp using HQPE sequence

Sequence HQPE Case	Stages	Brightness (%) Khar grass
1	H stage	55.95
	Q stage	56.17
	P stage	66.26
	E stage	68.12
2	H stage	55.19
	Q	57.27
	P stage	62.29
	E stage	66.71
3	H stage	58.71
	Q stage	60.27
	P stage	66.85
	E stage	72.61
4	H stage	62.73
	Q stage	69.21
	P stage	76.28
	E stage	80.24

Bleaching Results of khar grass Pulp using HQPE1 is shown below in Table VIII for increase of brightness with each stage.

Table VIII: Brightness of pulp using HQPE1 sequence

Sequence HQPE1	Stages	Brightness (%) Khar grass
1	H stage	55.10
	Q stage	69.24
	P stage	71.71
	E stage	76.24

3.8. Strength Properties

Burst index of paper samples varied from 0.50 to 0.62 $kPa.m^2/g$. The average value of 0.56 $kPa.m^2/g$ is suitable for writing grades, book printing, computer printing and newsprint paper. Tear index of paper samples varied from 3.40 to 3.53 $mN.m^2/g$. The average value of 3.48 $mN.m^2/g$ is good for average grades of writing and printing paper. Tensile index has values in between 24.0 to 25.20 N.m /g and the average

value is 24.60 N.m /g. So it is quite good considering such an indigenous pulp obtained from non-woody material. Further addition of 10-30% long fiber (as in usual practice in paper industries using short fiber pulp) in khar grass based short fiber stock will enhance all the strength properties significantly and make it suitable for good quality writing and printing.

3.9. Optical Properties

ISO brightness of unbleached pulp was between 24.88 to 26.80 % ISO. This is good and can be easily bleached to 80 – 85 % ISO brightness by conventional bleaching sequences.

4. Summary

Khar grass has a good potential to be a resourceful raw material for Cellulosic fibers.It may prove to be a major source of natural cellulosic fibersfor a number of industrial applications. The lignin percent (17.3%) in khar grass is lower than most of the conventional raw materials so it is easier to delignify. Catalyst (anthraquinon) concentration of 1% provides the best delignification, minimum kappa number and maximum holocellulose percentage in pulp. The liquor to straw ratio should be maintained at 10 for better results of delignification. The increase of temperature of reaction leads to decrease of Klason lignin percentage & decrease of kappa number of pulp significantly. Reaction time increase provides increase of delignification but time increase after 180 minutes is not adding any significant positive change. So three hours time is optimum. Weight average fiber length of pulp of khar grass is 0.88 - 1.0 mm which is good enough for manufacturing lower and average grade of papers. Brightness of unbleached acetic acid pulp hand-sheet was 26.8 % ISO which is average. Printing opacity of the pulp was very high (above 98%), which provides very good quality for writing and printing grades of paper.

5. References

[1] G. Chaturvedi, R. K. Jain, K. Singh, and A. G. Kulkarni. Indian Paper Industry – Growth and Prospects.*IPPTA J.*2006, 18 (2): 73-77.

[2] H. D. Kulkarni. Pulp and paper industry raw material scenario-ITC plantation a case study.*IPPTA J.*2013, 25 (1): 79-89.

[3] R. Bharati, S. Bharati, A. Sighal, and A. Sinha. Light microscopic studies of SaccharumMunja (Sarkanda) for paper making.*IPPTA J.*1994, Convention Issue 29-34.

[4] A. S. K. Sinha. Study of effects of process variables of rice straw delignification in catalyzed acetic acid medium at atmospheric pressure.*IPPTA J.*2008, 20 (2): 107-111.

[5] A. S. K Sinha, M. Singh, and S. P. Singh.Study on use of non-magnetic fraction of pulverized coal fly ash as filler in specialty paper manufacturing.*IPPTA J.*, 2010, 22 (2): 117-120.

[6] A. S. K Sinha.Effects of pulverized coal fly ash addition as wet end filler in paper making.*TAPPI J.*2008, 7 (9): 3-7.

[7] A. S. K. Sinha. Environment friendly removal of silica from wheat straw and SaccharumMunja using urea.*IPPTA J.*2012, 24 (3): 165-169.

[8] A. S. K. Sinha, M. Singh, and S. P.Singh.Acetic acid pulping and ECF bleaching of rice straw and effect of acid concentration on pulp characteristics.*IPPTA J.*2012, 24 (2): 151- 155.