Semi Close Loop System for Prehydrolysis Stage of Rayon Grade Pulping

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ABSTRACT

Prehydrolysis (PH) is prerequisite in selective removal of hemicelluloses during the production of rayon grade pulp. After prehydrolysis the liquor is either pumped to ETP for downstream processing or retained in the digester while processing for the kraft pulping. Draining the PH liquor to ETP indicates the water loss and discharge of enormous amount of pollution load. Performing the kraft pulping process along with prehydrolysate retained in the digester consumes higher active alkali and produces low pulp yield. Study has been carried out to provide technically superior and environmental friendly process for handling of prehydrolysate generated in rayon grade pulp mills. In this process prehydrolysate was concentrated by recycling it in the same process. Impact of recycling of prehydrolysate on pulping, bleaching and pulp properties were examined. Results indicate that recycling of prehydrolysate reduces water consumption by 35-43% during pulping and active alkali consumption by 1.5%. The suggested process increases the bleached pulp yield by 1.8%, whiteness by 1.2% and reduces impurities in the bleached pulp. The modified prehydrolysis process maintains the better pulp quality and provides significant economic advantages in rayon grade pulp mills.

Keywords: *Prehydrolysis, semi-close loop prehydrolysis, recycling of prehydrolysate, kraft pulping, rayon grade pulp.*

Introduction:

Rayon grade pulp contains high cellulose (>90%) and less impurities viz. ash, acid insoluble, calcium and iron etc. Prehydrolysis is prerequisite in selective removal of hemicelluloses during the production of rayon grade pulp. In the prehydrolysis stage low molecular weight carbohydrates are hydrolyzed to acids at high temperature. Water hydrolysis, vapour phase hydrolysis and acid boosted hydrolysis are the main types of prehydrolysis used to hydrolyze hemicelluloses prior to kraft pulping (Rudie 2007, Tripathi et al 2011). Large volume of water is being used in this stage. After prehydrolysis the liquor is either pumped to ETP for downstream processing or retained in the digester while processing for the kraft pulping.

Draining the prehydrolysate liquor (PH) liquor to ETP indicates the water loss and discharge of enormous amount of pollution load. COD of PH liquor of rayon grade pulp mill ranges between 80,000-125,000 mg/l. Studies has been conducted to utilize PH liquor as feed stock to bio-methanation process for production of methane gas, fermentation process for the production of n-butanol (Maddox and Murray 1983), xylitol (Converti 1999), succinic acid (Kim et al 2004) and ethanol (Kang et al 2011, Mendes et al 2011) etc. Though the above processes are technically feasible those are capital intensive and generate secondary pollution load.

Performing the kraft pulping process along with prehydrolysate retained in the digester consumes higher active alkali and produces low pulp yield. Study has been initiated with an objective of partially closing the prehydrolysis stage of rayon grade pulping by recycling the PH liquor. The paper describes the merits of semi close loop system for prehydrolysis stage and its impact on pulping, bleaching and pulp properties.

Experimental

Mixed hardwood chips collected from southern part of India were air dried and kept in the polythene bags to attain uniform moisture content which was determined as per the Tappi Test Method T 210 cm-03 before further processing of the chips.

Prehydrolysis and kraft pulping of chips was carried out in the autoclave digester consisting six bombs of 2.5 l capacity each, rotating in an electrically heated polyethylene glycol bath. For hydrolysis, the temperature was increased from ambient to 162 ^{0}C in 90 min, maintained at this temperature for desired period. Prehydrolysis liquor was drained from the bombs, and chips were further processed for kraft pulping. For semi close system this PH liquor was further used with desired amount of water in prehydrolysis stage. The PH liquor was recycled up to four times in the prehydrolysis stage.

The pulping conditions like time, temperature, bath ratio and sulphidity were maintained similar for all the experiments. Maximum cooking temperature was 160 ^{0}C. The temperature during pulping was increased from ambient to 160 ^{0}C in 90 min

and maintained at this temperature for 90 min. The unbleached pulp was screened in laboratory Somerville screen with 0.15 mm slot width. Screened unbleached pulp was cleaned in the laboratory centricleaner. The centricleaned pulp was tested for kappa number, yield, brightness and viscosity as per Tappi test methods T 236 om-99, T 412 om-02, ISO 2470 and Tappi T 230 om-04 respectively.

The unbleached pulp was bleached with $C_DE_{OP}HDE_P$ sequence followed by SO_2 treatment in the laboratory. Bleached pulps were characterized for brightness, CIE whiteness, L*a*b* values, yellowness and post color number using Technibrite Brightness Meter (Model TB 1c). Low molecular weight carbohydrates (hemicelluloses and degraded cellulose) were analysed by extracting the pulp with 10, 18 and 21.5% sodium hydroxide solution at 25°C for 1 h as per Tappi T 235 cm-00. Alpha cellulose and rayon yield of bleached pulp was determined using same methods. Bleaching experiments were performed under constant conditions as indicated below:

Particular	C_D-Stage	E_{OP}-Stage	H-Stage	D-Stage	E_P-Stage
Consistency (%)	3.0	10.0	10.0	10.0	10.0
Temperature (^{0}C)	amb	70	40	75	75
Time (min.)	45	120	120	180	120

Results and Discussion

Prehydrolysis and kraft pulping with retaining PH liquor in the digester

Prehydrolysis of the mixed hardwood chips was carried out with water prehydrolysis and the resultant prehydrolysate was retained in the digester during kraft pulping. Performing pulping process along with prehydrolysate required higher active alkali as part of the active alkali was consumed in neutralization of PH liquor. To produce unbleached pulp of ~ 15 kappa number and pentosan content ~3.5% mixed hardwood chips required 19% active alkali. Unbleached pulp yield of 38.2% was obtained at optimized prehydrolysis and kraft pulping conditions. Results of prehydrolysis kraft pulping are given in Table 1.

Table 1: Prehydrolysis and kraft pulping with retaining PH liquor in the digester

Parameter	Value
AA (%)	19
Unscreened yield (%)	38.5
Screen rejects (%)	0.3
Screened pulp yield (%)	38.2
Kappa number	14.8
Free alkali as Na_2O (g/l)	8.5
Pentosan in pulp (%)	3.4
Black liquor solids (%)	19.4

Prehydrolysis: temperature 162°C, time 105 min; Pulping: temperature 160°C, time 90 min.

Kraft pulping after draining PH liquor from the digester

Prehydrolysis of the mixed hardwood chips was carried out with water prehydrolysis and kraft pulping was performed after draining the prehydrolysate liquor from the digester. To produce unbleached pulp of ~ 15 kappa number and pentosan content ~3.5% mixed hardwood chips required 1.5% less active alkali (17.5%) compared to kraft pulping while retaining PH liquor in the digester. Unbleached pulp yield was also improved by 2.3%. Conditions of prehydrolysis kraft pulping and results thereof are given in Table 2.

Table 2: Prehydrolysis and kraft pulping after draining PH liquor from the digester

Parameter	Value
AA (%)	17.5
Unscreened yield (%)	40.9
Screen rejects (%)	0.4
Screened pulp yield (%)	40.5
Kappa number	15.8
Free alkali as Na_2O (g/l)	6.4
Pentosan in pulp (%)	3.6
Black liquor solids (%)	18.4

Prehydrolysis: temperature 162°C, time 105 min; Pulping: temperature 160°C, time 90 min.

Semi close loop system for prehydrolysis stage

Performing kraft pulping after draining the PH liquor was good for pulp production but it led to generate huge amount of pollution load to environment. As discussed earlier several options are available to convert PH liquor for value added products and reduction in generation of pollution load. In the current approach, the PH liquor generated was reused along with the fresh water in prehydrolysis stage itself. Recycling of the PH liquor was studied up to three cycles. Result indicated that concentration of PH liquor was increased to 7.6% from initial 5.6% after three times recycling of prehydrolysate. After attaining certain concentration of prehydrolysate liquor it can be routed to chemical recovery loop with proper chemical treatment. Recycling of prehydrolysate did not

Table 3: Effect of prehydrolysate recycling on prehydrolysis kraft pulping

Particular	No recycle	Once recycle	Twice recycle	Thrice recycle
	Prehydrolysis			
Fresh water taken (m^3/t)	2.7	1.5	1.5	1.5
PH taken (m^3/t)	0.0	1.2	1.2	1.2
Liquor pH	3.1	3.1	3.2	3.1
PH volume generated (m^3/t)	1.2	1.2	1.2	1.2
Solids (%)	5.6	6.8	7.2	7.6
	Pulping			
AA (%)	17.5	17.5	17.5	17.5
Kappa no	15.8	15.7	15.8	15.7
Unscreened pulp yield (%)	40.9	40.7	40.8	40.8
Screen rejects (%)	0.3	0.4	0.4	0.5
Screened pulp yield (%)	40.5	40.3	40.4	40.3
Pantosans (%)	3.6	3.6	3.6	3.5
Free alkali (gpl) as Na_2O	6.4	6.4	6.5	6.2
Black liquor Solids (%)	18.4	19.2	19.4	19.5

Prehydrolysis: temperature 162°C, time 105 min; Pulping: temperature 160°C, time 90 min., AA 17.5%

affect the pulp properties like kappa number, pulp yield and pentosans content in pulp. Unbleached pulp yield increased when pulping was performed with recycling of PH liquor as compared to pulping performed with retaining the prehydrolysate in the digester (Figure 1). Results of PH liquor recycling on prehydrolysis kraft pulping are given in Table 3.

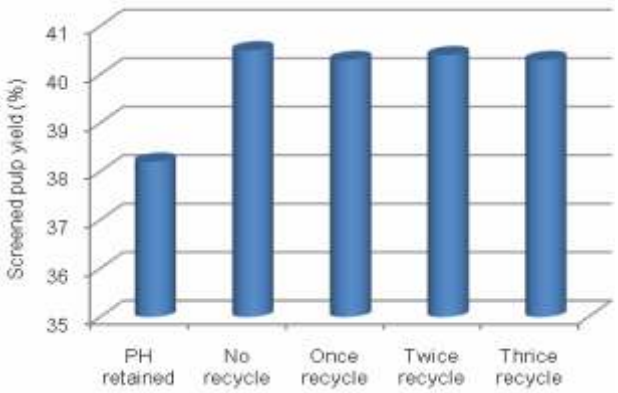

Figure 1: Effect of prehydrolysate recycling on unbleached pulp yield

Bleaching of pulp produced with semi close loop system

Unbleached pulps produced were bleached with $C_DE_{OP}HDE_P$ sequence followed by SO_2 treatment. Pulp produced with recycling of prehydrolysate showed better bleaching response as compared to pulp produced while retaining the PH liquor in the digester during pulping. Using same chemicals during bleaching the whiteness obtained in the pulps produced with recycling of PH liquor in prehydrolysis stage was better as compared to pulps produced with retaining PH liquor in the digester while pulping (Figure 2). Results of bleaching of pulp are given in Table 4.

Table 4: Bleaching of semi close loop system for prehydrolysis kraft pulps

Parameter	PH retained	No recycle	Once recycle	Twice recycle	Thrice recycle
Kappa number	14.8	15.8	15.7	15.8	15.7
		Cl_2 stage			
Kappa factor	0.22	0.22	0.22	0.22	0.22
End pH	2.1	2.1	2.2	2.2	2.2
		E_{OP} stage (NaOH added 2.0%)			
CE Kappa no.	2.1	2.1	2.2	2.1	2.1
CE Brightness (%)	59.6	60.4	61.0	61.3	61.0
		H stage *(Hypo added 0.6%)*			
Hypo consumed (%)	0.44	0.44	0.30	0.31	0.30
Brightness (%)	82.0	82.6	82.6	82.4	82.7
		D stage (ClO_2 added 0.8%)			
ClO_2 consumed (%)	0.73	0.73	0.72	0.73	0.73
Brightness (%)	86.9	87.2	87.5	87.5	87.6
		E_P stage *(NaOH added 0.6%, H_2O_2 added 0.3%)*			
Brightness (%ISO)	90.2	90.4	90.6	90.6	90.5
CIE Whiteness	80.52	81.21	81.44	81.46	81.41
ASTM Yellowness	5.06	4.89	5.00	4.98	4.87
L*	97.45	97.67	97.56	97.70	97.61
a*	-0.18	-0.23	0.22	-0.21	-0.19
b*	2.95	2.62	2.67	2.35	2.60
Bleached pulp yield (%)	36.3	38.4	38.2	37.9	38.1

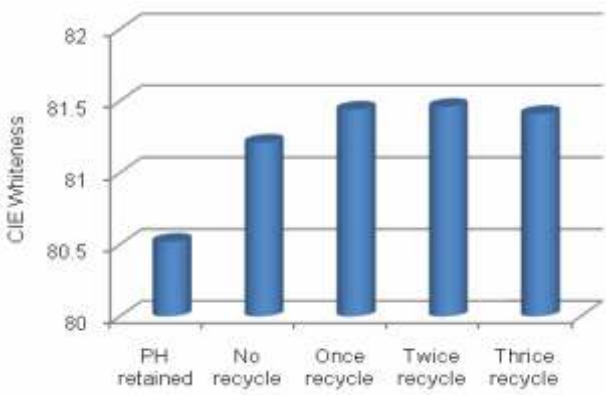

Figure 2: Effect of PHL recycling on whiteness of pulp

Table 5: Ash analysis results of bleached rayon grade pulp

Parameter	PH retained	No recycle	Once recycle	Twice recycle	Thrice recycle
Ash content (%)	0.065	0.059	0.054	0.051	0.050
Acid insoluble (ppm)	120	110	105	110	105
Silica (ppm)	100	95	95	90	90
Calcium (ppm)	50	55	50	50	50
Iron (ppm)	10	15	10	10	7

Ash content, acid insoluble and silica in the bleached pulps produced with recycling the PH liquor was less as compared to these in the pulp produced while retaining PH liquor in the digester during pulping. Characteristics of the ash of bleached rayon grade pulp produced with and without recycling the prehydrolysate are given in table 5. Acidic prehydrolysate acts as the solubilizer of insolubles, silica and metal ions etc. during prehydrolysis. Regulation of pentosans in pulp can be better managed by the recycling of PH liquor due to its acidic nature.

Conclusion

Recycling of prehydrolysate liquor reduced water consumption by 35-43% during pulping and active alkali consumption by 1.5%.

Semi close loop system for prehydrolysis stage provides environmental friendly process to deal with prehydrolysate generated in rayon grade pulp mills.

Recycling of prehydrolysate liquor improved the bleached pulp yield by 1.8%, enhanced whiteness and other pulp properties.

The modified prehydrolysis process maintains the better pulp quality and provides significant economic advantages in rayon grade pulp mills.

Referencess

- Converti A., Perego P., Dominguez J.M. (1999). Xylitol production from hardwood hemicellulose hydrolysates by Pachysolen tannophilus, Debaryomyces hansenii, and Candida guilliermondii. Applied Biochemistry and Biotechnology, 82 (2), pp 141-151.
- Kang L., Webster D., Cullinan H., Lee Y. Y (2011). Ethanol Production from the Mixture of Hemicellulose Pre-hydrolysate and Paper Sludge. BioPro Expo &

Marketplace / Atlanta, GA / March 14-16, 2011.

- Kim D.Y., Yim S.C., Lee P.C., Lee W.G., Lee S.Y., Chang H.N. (2004). Batch and continuous fermentation of succinic acid from wood hydrolysate by Mannheimia succiniciproducens. Enzyme and Microbial Technology, 35 (6-7), pp 648-653.
- Maddox I.S. and Murray A.E. (1983). Production of n-butanol by fermentation of wood hydrolysate. Biotechnology Letters, 5 (3), pp175-178.
- Mendes C.V.T., Rocha J.M.S., Sousa G.D.A., Carvalho V.S. (2011). Extraction of hemicelluloses prior to kraft cooking: a step for an integrated biorefinery in the pulp mill. O Papel, 2(9), pp. 57-61.
- Rudie A., Reiner R., Ross N., Kenealy W. (2007). Acid Prehydrolysis of Wood. Proceedings of TAPPI engineering, pulping and environmental conference, Jacksonville, FL: Atlanta, pp 37.
- Tripathi S., Mishra O.P., Sharma N., Chakrabarti S.K., Varadhan R. (2011). Quality improvement of rayon grade bamboo pulp by modified bleaching. Journal of Korea TAPPI 43 (2), pp 1-8.