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THE INFLUENCE OF LIGNIN REMOVAL ON THE ENERGY BALANCE OF FUTURE PULP MILLS

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SUMMARY

Kraft pulp mills have a desire to increase their production capacity. For recovery boiler limited mills, an established technology, the lignin removal from black liquor is an alternative to decrease the recovery boiler load. Lignin removal decreases the organic content of black liquor, but the inorganic portion remains essentially unchanged. Balances are performed to show how lignin removal affects pulp mill operation. A modern South American pulp mill served as a base case model for 1.5M Adt/a production level. The target is to verify modifications so that pulping and chemical recovery processes are not negatively affected. Future mills can thus be made cheaper and with a smaller recovery boiler. An energy balance is also performed for each case in order to check the influence of lignin removal on the steam generation and utilization rates. The results show that the steam generation from recovery boiler is decreased by 21% by removing 30% of lignin from black liquor. For the same removal rate, the fuel heating value is decreased by 8.5% and the recovery boiler required capacity by 10.2%. The total electricity output is decreased by 54MW.

Keywords: black liquor, lignin removal, recovery boiler

INTRODUCTION

The wood to be pulped normally consists of cellulose 40-50 %, hemicellulose 23-32 %, lignin 15-30 % and extractives 2-5 %. About half of the original wood is converted to kraft pulp and the rest of the organics in wood are led through evaporation plant to energy production in recovery boiler. The separation of lignin is an option that is considered by the pulp mills for several reasons. Firstly, the flue gas side capacity of the recovery boiler is often a bottleneck that limits pulp production. Removing part of the lignin from the black liquor decreases the heat load on the recovery boiler and more pulp can be produced [1]. Secondly, the separated lignin could be used to replace e.g. fuel oil or natural gas in the lime kilns or be combusted in a power boiler if required.

Thirdly the modern pulp mills have energy surplus that often is exported as electricity and biofuels, e.g. bark. Separated lignin adds another option in the form of renewable biofuel. Fourthly separated lignin can be used as a raw material in chemicals [2]. Refined lignin has the potential of being a raw material for several new products such as carbon fibres/materials, phenols, adhesives/binders, dispersant and metal chelating agents [3]. A lignin extraction process may also serve as an option to remove certain non-process components, such as silica and aluminium.

There are currently two interesting methods being used to remove lignin from black liquor: ultrafiltration in the digester [4], and acid precipitation in the evaporation plant [5,2,6]. The precipitation method is the technology mentioned in this work and is shown in figure 1. Black liquor is led from evaporation in 30-40% dry solid content to the precipitation vessel. The success of precipitation process is dependent on pH and temperature. The hydrogen source can be either sulfuric acid or CO_2. Sulphuric acid is easy to handle in the mixing stage but the sulphur balance in the mill can be affected. The use of CO_2 avoids this balance problem but the mixing stage is more complicated. The lignin precipitate is filtered and then washed to purify the product. The reminder of the black liquor is returned to the chemical recovery system in the pulp mill.

Extracting lignin from black liquor may be an opportunity for decreasing its viscosity. Effect of lignin removal to black liquor BPR has been studied by Moosavifar et al.[7]. They concluded that there was little effect on boiling point rise.However, the operation of recovery boiler can be negatively affected if lignin removal rate is too high (figure 1). Some balances have been developed to evaluate the influence of lignin removal on recovery boiler operation [1, 8] and on the energy savings of pulp mills [9].

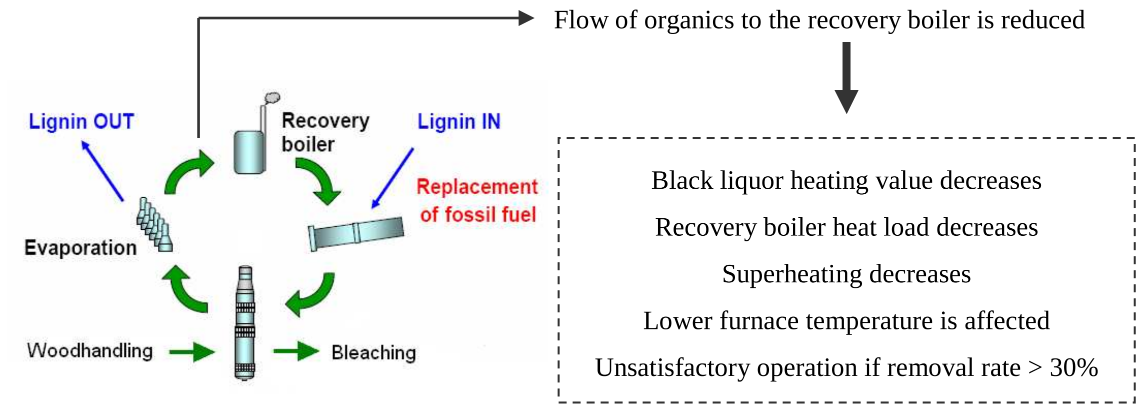

Figure 1. Lignin removal and its implications regarding recovery boiler performance

Removal of lignin reduces the heat available at furnace, figure 2. The portion of the heat in black liquor needed for reduction increases. Therefore the net heat available in furnace per unit mass of black liquor decreases even more. It can be seen that at high lignin removal rates the heat available at furnace is less than is typical for black liquors.

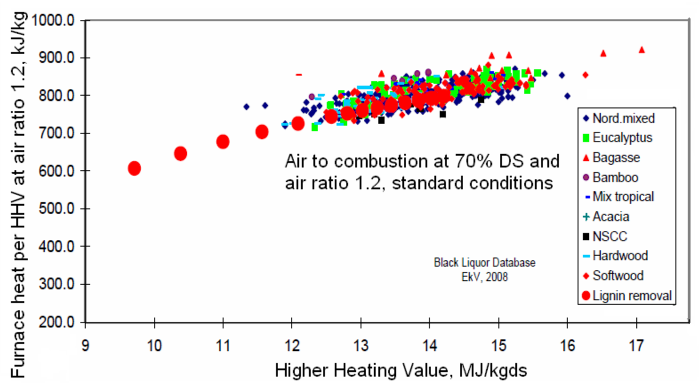

Figure 2. Furnace heat at various lignin removal rates compared to general trend in black liquors [1]

Predictions for lower furnace temperature and ash generation indicate that at lignin removal rate of about 50 %, furnace behaviour starts deviating significantly from those conditions that normally occur in recovery boilers [1]. As the higher heating value of lignin removed black liquor falls below 11 MJ/kgds, the mill operational data does not exist anymore. So therefore these predictions should be looked more as trends and not as absolute values.

It was possible to conclude that lignin removal does not affect significantly the burning properties of black liquor. Even though for the same heat requirement more black liquor needs to be burned, the air and flue gas flows are close to the original values. Current recovery boilers are therefore suitable for lignin removed liquor combustion without significant retrofits.

MILL BALANCE

In order to evaluate the influence of lignin removal on certain operational variables, calculations were performed using a detailed pulp mill balance developed in excel format. Since thousands of variables and calculations are involved, tools for tracing the dependent variables become important. This feature makes excel particularly user friendly for the current task. A modern eucalyptus pulp mill in South

America served as a base case model and a balance for 1.5M Adt/a was done. The balances show the consequences of lignin removal on the recovery process operation and energy generation. Non-process elements such as Cl and K in black liquor may affect the operation of chemical recovery process [10]. It is then interesting to take them into consideration. Three different contents of Cl and K in black liquor were initially considered: 1) Cl=0.4%wt, K=1.2%wt, 2) Cl=0.6%wt, K=1.6%wt, 3) Cl=1.0%wt, K=1.6%-wt. We will see that the composition of black liquor changes when lignin is removed. The balance is calculated with regard to the following major assumptions:

- Active alkali fixed as 138.1 gNaOH/l.
- Wood composition: Cellulose 46%, hemicellulose 25%, lignin 26%, extractives 3%.
- Fixed value for sulfidity:32%; and fixed value for reduction: 96%
- Formation rate of thiosulphate and sulfite compounds are fixed
- Weak black liquor concentration fixed at 15.3%
- Strong black liquor concentration fixed at 80.0%
- Operation hours: 350 days or 8400 hours per year

RESULTS AND DISCUSSION

As organics are reduced but inorganics remain the same, more lignin removed solids needs to be fired for the same steam load. On the other hand, if the reduction of steam production is taken as an alternative, some parameters of chemical recovery process are affected. Table 1 shows some variables of the chemical recovery process if 30% of lignin is removed from black liquor. The values are calculated by considering Cl=0.4% wt; K =1.2% wt in black liquor when lignin removal rate is zero.

Table 1. Some variables for different rates of lignin removal

Variable	Percentage of lignin removal				
	Unit	0%	10%	20%	30%
Dry solids in BL after lignin removal	kg/Adt	1353.2	1307.2	1261.1	1215.1
White liquor density	kg/m^3	1144.0	1143.9	1143.8	1143.7
White liquor flow	m^3/h	547.9	547.9	547.9	547.9
Total inorganics to black liquor	kg/Adt	437.2	437.3	437.3	437.3
Total organics to black liquor	kg/Adt	915.9	869.9	823.8	777.7
Lignin in black liquor	kg/Adt	460.7	414.6	368.5	322.5
Black liquor HHV	MJ/kg	14.30	13.94	13.55	13.14
Heat into recovery boiler	MW	892.3	840.3	788.2	736.2
Weak black liquor flow	m^3/h	1483.2	1483.2	1483.2	1483.2
Black liquor flow to furnace	tDS/d	5991.0	5787.5	5583.6	5379.7
Smelt flow	kg/kgDS	0.425	0.436	0.447	0.460
Evaporation load	t_{H2O}/h	1310.6	1322.6	1334.7	1346.8
- Steam consumption	t/h	218.5	222.1	223.7	225.2
- Cooling water flow	m^3/h	13834	13961	14088	14216
Power generation	MW	198.5	180.3	162.2	143.7

(a) – According to design values (not operational)

The highest impact of lignin removal is on the recovery boiler process because of changes in fuel properties. The consequence is a high impact on the power generation. Minor impacts can be observed in the evaporation plant.

Effects on black liquor properties

As mentioned before, the decrease in the organics flow to recovery boiler will decrease the heat load into the furnace. The decrease in fuel high heating value is the main reason. If lignin is removed from black liquor, we will have, approximately, the following changes in the black liquor composition:

Table 2. Changes in black liquor composition (initially, Cl=0.4% wt; K =1.2% wt)

Variable	Percentage of lignin removal				
	Unit	0%	10%	20%	30%
Carbon (C)	%-wt	34.97	34.18	33.33	32.41
Hidrogen (H)	%-wt	3.43	3.35	3.27	3.18
Nitrogen (N)	%-wt	0.10	0.10	0.10	0.10
Sulphur (S)	%-wt	3.79	3.93	4.07	4.22
Sodium (Na)	%-wt	20.70	21.17	21.69	22.23
Potassium (K)	%-wt	1.20	1.23	1.26	1.30
Chloride (Cl)	%-wt	0.40	0.41	0.42	0.43
Oxygen by difference	%-wt	35.41	35.63	35.87	36.12
Inorganics		26.09	26.74	27.44	28.18

Table 2 shows that the ratio of carbon to hydrogen remains fairly constant. Therefore the combustion of organics will not change too much even if lignin is removed from the black liquor. On the other hand, the lignin removal has a high impact on the fuel heating value, figure 3. The method for calculating the black liquor high heating value is well described in the literature [11].

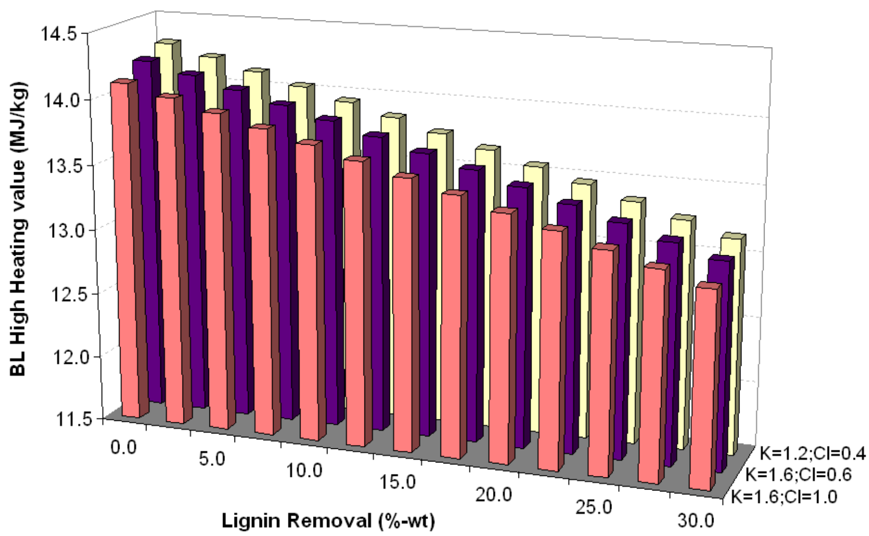

Figure 3. Effect of lignin removal on the black liquor heating value

Effects on evaporation load

More research is needed to study the influence of lignin removal on evaporation load. The water balance has an important role on the operation and design of the evaporation capacity. In the balance, it is assumed that the pulp dilution water in the washing process is fixed. Then the weak black liquor flow to evaporation plant remains constant. However, figure 4 shows that there is a slightly increase in the required capacity of evaporation. The reason is that this capacity is a variable dependent of the total solid flow to the recovery boiler, which decreases if the lignin removal rate increases.

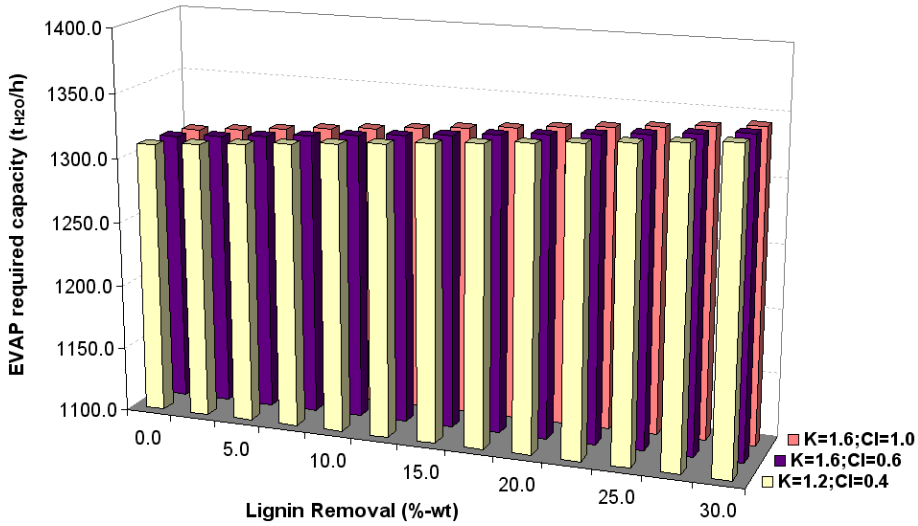

Figure 4. Effect of lignin removal on the required capacity of the evaporation plant (1.5M ADt/a)

The required capacity is increased by about 3% if 30% of lignin is removed from black liquor. This means that the steam and cooling water consumption in evaporation stage increases at the same rate.

Effects on recovery boiler performance

The recovery boiler is the most costly equipment in chemical recovery system. Designing for a lower capacity boiler can represent some millions of € in savings. Figure 5 shows that this is possible. However, the reduction in steam generation is significant, as can be seen from figure 6. This makes the electricity production decrease by about 26% if 30% of lignin is removed from black liquor. Then less surplus electricity is available. More details about power generation can be seen in the next section.

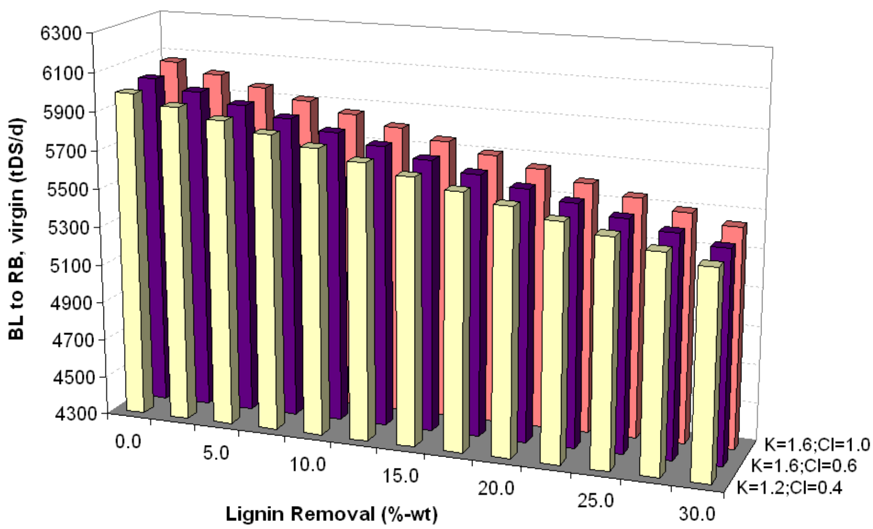

Figure 5. Effect of lignin removal on the black liquor flow to recovery boiler (1.5M Adt/a)

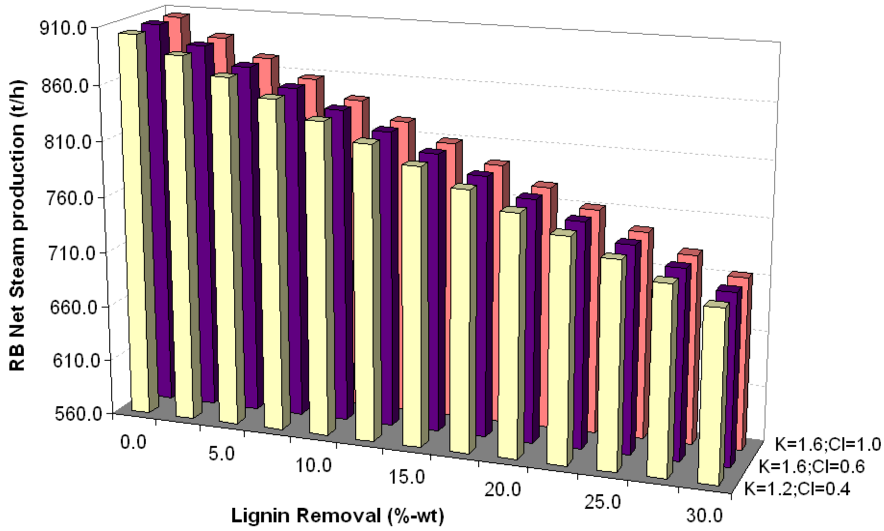

Figure 6. Effect of lignin removal on the recovery boiler steam production (1.5M Adt/a)

Effects on the power generation

The decrease in steam production from recovery boiler will decrease the electricity generation. This trend can be observed in figure 7. For the electricity output calculation, the following design conditions were considered:

- Low pressure steam: 3.3bar(g) and 155ºC
- Medium pressure steam I: 11bar(g) and 200ºC
- Medium pressure steam II: 35bar(g) and 370ºC (sootblowing)
- High pressure steam from the boilers: 85bar(g) and 485ºC
- Biomass boiler capacity: 204 t steam/h
- One back-pressure turbine (extraction of MPI, MPII and LP)
- One steam condensing turbine (extraction of LP steam)
- Two generators of same capacity

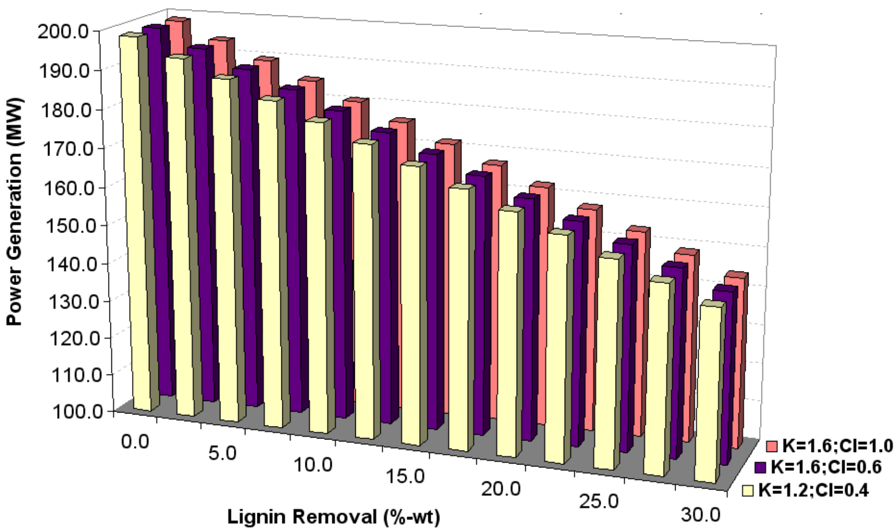

Figure 7. Effect of lignin removal on the power generation (1.5M Adt/a)

Table 3 shows that it is still possible to generate surplus electricity after removing 30% of lignin from the black liquor. However, according to the energy balance, the biomass boiler is indispensable to achieve such goal.

Table 3. Some variables for different rates of lignin removal

Variable	Percentage of lignin removal				
	Unit	**0%**	**10%**	**20%**	**30%**
Biomass boiler steam production	t/h	204	204	204	204
Recovery boiler steam production	t/h	903.5	840.0	776.6	713.1
Power generation	MW	198.4	180.3	162.2	143.7
Electricity usage	MW	108.7	108.3	107.9	106.7
Electricity to be sold [(a)]	MW	89.7	72.0	54.3	37.0

(a) – According to design values

Designing a 1.5M ADt/a pulp mill

Pulp mills have the desire to run the pulp mill with flexibility. It means that lignin removal process has to come as an alternative. Depending on the fluctuations of lignin or electricity prices, the pulp mill can decide whether they want to run the mill with or without the lignin removal system. Taking this issue into consideration, it would be appropriate to design a pulp mill with full capacity, i.e., without removing lignin from black liquor. Moreover, there are no references for new kraft pulp mills with lignin removal system, which can discourage new investments with such technology.

It is important to mention that disturbances in the recovery boiler become an important issue if lignin removal rate is too high. Figure 8 shows the designed capacity of one large pulp mill. The changes in the required capacity of recovery boiler, as well as in the power generation, are based on maximum lignin removal rate of 30%.

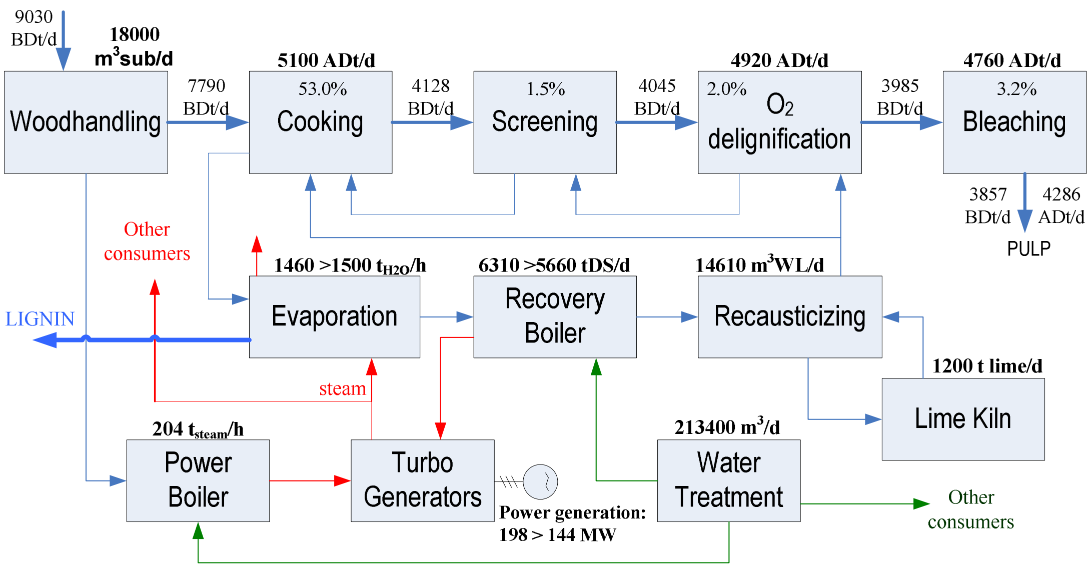

Figure 8. Design of 1.5M Adt/a pulp mill, with and without lignin removal system

The energy balances show that, without the operation of biomass boiler, the lignin removal rate is limited to about 13%. More lignin removal than that, the steam flow demand would be higher than the steam generated by the recovery boiler. Table 3 shows that the biomass boiler enables significant production of surplus electricity. However, the energy efficiency of the process depends on the strategy defined by the pulp mill. The investment and operational costs will vary according to the number of effects used in the evaporation plant, strategy adopted for the feedwater pre-heating system, etc. The steam temperature and pressure are also important. However, in recovery boilers, high parameters are susceptible to corrosion problems. In addition, as mentioned before, the decision to run a biomass boiler will strongly affect the energy balance. In this case, the government incentives can play a vital role by providing credits for the production of clean energy. The decision to invest in lignin removal system depends on the price of electricity, price of lignin, investment cost, etc. If technologies are available to produce chemicals from lignin, its price will surely increase. Another option is to use lignin as an alternative fuel in lime kilns.

CONCLUSIONS

This work shows that it is possible to make new mills with smaller recovery boiler. However, a successful case with lignin removal system depends on the overall energy balances and economic aspects. Prices of lignin, fuels and electricity, as well as operation and investment costs are important issues to be considered.

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REFERENCES

1. E. Vakkilainen, E. Välimäki, “Effect of Lignin Separation to Black Liquor and Recovery Boiler Operation”, TAPPI Engineering, Pulping & Environmental Conference, October 11-14, 2009.

2. F. Öhman, H. Wallmo, and H. Theliander, “A Novel method for washing lignin precipitated from kraft black liquor – Laboratory trials”, *Nordic Pulp and Paper Research Journal*, Vol. 22, No. 1, 2007, pp. 9 - 16.

3. P. Axegård, B. Backlund, P. Tomani, 2007, The pulp mill based biorefinery. Presentation at PulPaper June 6-7 Helsinki 2007.

4. O. Wallberg, A. Holmqvist, Ann-Soft Jönsson, “Ultrafiltration of kraft cooking liquors from a continuous cooking process”, *Desalinatio*n Vol. 180, pp 109-118, 2005.

5. F. Öhman, and H. Theliander, 2007, Filtration properties of lignin precipitated from black liquor. *Tappi Journal*, Vol. 6, No. 7, pp. 3 – 9, 2007.

6. H. Wallmo, H. Theliander, “The influence of hemicelluloses during the precipitation of lignin in kraft black liquor”, *Nordic Pulp and Paper Research Journal* Vol 24, pp 165-171, no. 2, 2009

7. A. Moosavifar, P. Sedin, H. Theliande, “Viscosity and boiling point elevation of black liquor: Consequences when lignin is extracted from black liquor. Nordic *Pulp and Paper Research Journal*, Vol. 21, No. 2, pp. 180–187, 2006.

8. E. Välimäki, P. Niemi, K. Haaga, “Effect of A Case Study on the Effects of Lignin Recovery on Recovery Boiler Operation”, International Chemical Recovery Conference, April 2010.

9. C. Laaksometsä, E. Axelsson, T. Berntsson, A. Lundström, “Energy savings combined with lignin extraction for production increase: case study at a eucalyptus mill in Portugal”, *Clean Techn Environ Policy, Vol.*11, pp 77–82, 2009.

10. M. Hamaguchi, E. Vakkilainen, “Influence of Cl and K on the operation and design of chemical recovery equipment”, International chemical recovery conference, 2010.

11. T. Adams, J. Frederick, “Kraft Recovery Boiler Physical and Chemical Processes”. American Paper Institute, p. 55, 1988.