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Black Liquor Oxidation As a Means of Efficient Chemicals Recovery in Paper Mills †

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Abstract: Chemicals recovery cycle is essential for every pulp mill producing pulp by chemical pulping. Its purpose is to recover inorganic chemicals used for pulping with the possibility of heat and electric energy cogeneration. New methods, such as white liquor oxidation or black liquor gasification can increase the efficiency of the cycle and help to decrease chemicals consumption, thus contributing to more environmentally friendly pulp and paper production. This work is focused on assessing white liquor processing methods and on evaluating the impact on chemicals consumption in further pulp processing stages. Model balances are set up for a large paper mill with a capacity of 0.75 mil. tonnes of pulp and paper production, requiring around 100 tonnes per hour white liquor for pulping. Results indicate that a major saving can be realized on chemicals purchase: more than 0.8 tonnes per hour and more than 1.2 tonnes per hour of pure sodium hydroxide in case of partial white liquor oxidation and full white liquor oxidation, respectively. Greenhouse gases emissions can be reduced by more than 10 thousand tonnes per year of CO_2 equivalent as a result. Economics of proposed technology implementation is favorable, indicating a simple payback period of less than three years for a certain combination of chemicals and utilities costs.

Keywords: recovery cycle; white liquor; oxidation; pulping

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1. Introduction

The ongoing climate change stresses the need for finding and implementing solutions for sustainable low-carbon industrial production. This includes switching to low-carbon energy sources and restructuring industry to implement new technologies and processes with lower energy and material consumption and wastes and emissions release [1]. Heavy industry, including pulp and paper production, is a major contributor to industrial emissions; thus, it is a priority to focus the innovation on these sectors [2]. Large-scale continuous processes operated in this sector enable reaching large absolute savings in energy and material consumption even with a small incremental process improvement.

Chemical pulp mills producing kraft pulp consume big amounts of white liquor for the wood chips cooking process. Significant amount of fresh sodium hydroxide is also needed to improve Na-S balance in white liquor and for oxygen delignification and some is used in the bleaching stages as well [3]. Apart from economic expenditures, NaOH consumption contributes to carbon footprint of pulp mills, by 0.63 to 1.91 tonnes CO_2 equivalent per ton of consumed crystalline NaOH, depending on its production technology and its calculation assumptions [4,5].

Novel technologies of liquor oxidations (white liquor, green liquor, but also black liquor) are currently used in some pulp mills and are under development. White liquor is oxidized for it to be later used as a source of caustic in oxygen delignification and alkali extraction stages in the bleach plant [6]. The degree of oxidation, yielding either a partially or fully oxidized white liquor, determines where the liquor can be used.

This contribution aims at developing conceptual white liquor balances of a large-scale paper mill in base state and in two cases applying either partial or full white liquor oxidation. As a result, the potential for sodium hydroxide consumption reduction is quantified and the associated greenhouse gases emissions reduction is estimated. Economic evaluation is performed to estimate the required investment and operational costs and to evaluate the economic feasibility of the proposed technology implementation. Thereby, a contribution towards cleaner and more sustainable industrial production is presented.

2. Materials and Methods

White liquor represents the supply of cooking chemicals for wood chips cooking in digester. The active chemicals in kraft pulping are hydroxide and hydrogen sulphide ions, OH^- and HS^- [3]. Hence, the white liquor is a mixture of sodium hydroxide and sodium sulphide in water. The considered composition of white liquor is shown in Table 1.

Table 1. Composition of white liquor, adopted from [7].

Component	Concentration (g/l)	Mass fraction (-)
NaOH	90	0.0783
Na_2S	39	0.0339
Na_2CO_3	26.2	0.0228
Na_2SO_4	8	0.0070
$Na_2S_2O_3$	4	0.0035
Na_2SO_3	0.9	0.0008

Partially oxidized white liquor can be produced by oxidation of sodium sulphide contained in the white liquor with oxygen from air to thiosulphate [3,8], (1).

$$2\ Na_2S + 2\ O_2 + H_2O \rightarrow Na_2S_2O_3 + 2\ NaOH \quad (1)$$

The sulphide conversion into thiosulphate can be in this case up to 97 – 98 % [6]. Partially oxidized white liquor is suitable for the oxygen delignification process [3,6]. In this study, sulphide conversion into thiosulphate of 98 % is assumed and the reaction consumes 80 % of the oxygen supplied to the reactor. Oxygen supply is ensured by an air compressor (isentropic efficiency 90 % and mechanical efficiency 95 %), which compresses air from atmospheric pressure to 2 bar (a). The air used as the oxygen source has a temperature of 15 °C, a pressure of 98 kPa and a relative humidity of 80%.

Fully oxidized white liquor can be produced by oxidation of white liquor with pure oxygen in pressurized reactors if the residence time and temperature of the white liquor are increased [3]. In this case, together with the previous equation (1) further oxidation reaction (2) takes place [6,8].

$$Na_2S_2O_3 + 2\ O_2 + 2NaOH \rightarrow 2\ Na_2SO_4 + H_2O \quad (2)$$

In this oxygen-based system, the sulphide conversion into thiosulphate can be 98 – 99 % and the sulphide conversion into sulphate can be up to 60 % [6]. Fully oxidized white liquor can be also used for the oxygen delignification process, but it can also be useful for the peroxide bleaching stages and gas scrubbing applications. Total oxidation of white liquor is performed in a pressurized reactor using pure oxygen. In the reactor, reactions (1) and (2) take place with conversions of sodium sulphide and sodium thiosulphate of 98 % and of 60 %, respectively. As the system is pressurized, the pressure of fed oxygen is set to 6 bar (a). It is assumed that the reactions consume 97 % of the oxygen supplied to the reactor. Energy consumption of pure oxygen production represents 0.5 kWh/Nm^3 of produced oxygen [9]. To compare the compositions of basic white liquor (BWL), partially oxidized white liquor (POWL) and totally oxidized white liquor (TOWL), the following parameters (composition indicators) are calculated (3) – (5) [10], with concentrations of each compound based on NaOH equivalent. The considered density of all white liquors is 1150 kg.m^{-3} [10].

$$\text{Active Alkali (AA)} = c(\text{NaOH}) + 12\ c(\text{Na}_2\text{S}) \quad (3)$$

$$\text{Effective Alkali (EA)} = c(\text{NaOH}) + c(\text{Na}_2\text{S}) \quad (4)$$

$$\text{Sulfidity (S)} = 100\ \text{c}(\text{Na2S})/\text{AA} \quad (5)$$

Figure 1 presents the white liquor oxidation technology and highlights possibilities for chemicals replacement.

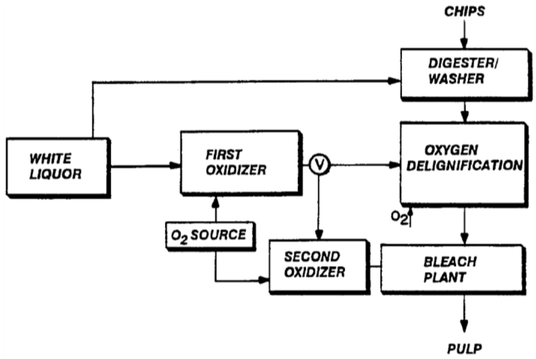

Figure 1. Schematic depiction of white liquor oxidation technology integration in a paper mill. Source: Own elaboration.

Real plant operational data presented in [11] allow quantification of material streams involved: the model pulp mill with the production of about 13,000 tonnes of bleached pulp per day consumes about 3.5 t/h (tonnes per hour) of fresh sodium hydroxide solution (concentration of 120 g/l) together with 5.8 t/h of white liquor and 1.1 t/h of pure oxygen. In the "EO" bleaching section (alkaline stage), 4 t/h of fresh sodium hydroxide is used together with 0.04 t/h of pure oxygen for pulp bleaching. Another 4 t/h of fresh sodium hydroxide is used in the peroxide bleaching stage. Total amount of potentially replaceable sodium hydroxide represents 11.5 t/h, out of which 7.5 t/h can be replaced by partially oxidized white liquor and further 4 t/h (peroxide bleaching) can be replaced by fully oxidized white liquor.

Table 2. Costs of materials and utilities.

Material / Utility	Cost (EUR)	Unit	Reference
Electricity	100	MWh	[14]
NaOH pure (crystalline)	150 to 500	t	[15]

Key equipment investment cost estimation followed the exponential method used to estimate the investment cost of equipment or plant based on existing cost data of the same equipment with different capacity with the well-known "six tenths rule" applied to the exponent value [12]. Indexation by Chemical Engineering Plant Cost Index (CEPCI) was used to recalculate investment costs of past investment to current conditions [13]. The factor method is used for the estimation of total investment cost (TIC) of a plant with TIC being assumed as key equipment investment cost multiplied by a factor of 5 [13] recommended for liquids-handling plants installed within existing industrial area. Assumed materials and utilities costs are summed up in Table 2; 8500 working hours per year are considered.

3. Results

3.1. Comparison of white liquors composition

Composition indicators of BWL, POWL and TOWL are compared in Table 3.

Table 3. Composition indicators of basic white liquor (BWL), partially oxidized white liquor (POWL) and totally oxidized white liquor (TOWL).

Composition indicator	BWL	POWL	TOWL
Active alkali (g/l)	130.0	110.0	97.5
Effective alkali (g/l)	110.0	109.5	96.0
Sulfidity (%)	30.76	2.70	3.05

As shown in Table 3, values of AA and EA are somewhat lower in oxidized liquors, compared to BWL. Sulfidity in oxidized liquor is much lower than in BWL. If the sulfidity is too low, the lignin content of the pulp may be relatively high and carbohydrate degradation may be severe which leads to low pulp strength. However, if the sulfidity is too high, emissions of reduced sulphur compounds may increase and corrosion rates in the recovery process may be high [3].

3.2. White liquor oxidation

Mass balance of bleaching plant yielded potential for NaOH solution (concentration of 120 g/l) replacement by POWL of 7.5 t/h, corresponding to 0.8 t/h of crystalline NaOH. A potential for NaOH solution replacement by TOWL, obtained by bleaching plant balance amounted to 11.5 t/h, being an equivalent of 1.2 t/h of crystalline NaOH. Annually it can be up to 7 – 10 thousand tonnes of sodium hydroxide saved, resulting in a decrease of paper mill´s carbon footprint related to purchased chemical by 6 to 19 ktons of CO_2 annually. Considering paper mill's production of 13 kton per day this would translate into 0.01 to 0.03 tons of CO_2 per ton of produced pulp.

A substantial economic effect is achieved as a result. Crystalline NaOH prices varied between 150 and 500 EUR per ton in Europe in last few years [15]. Achievable annual saving amounts, thus, to 1 to 5 mil. EUR.

3.2. Economic parameters

Basic economic parameters are estimated for three plant variants. They include POWL plant, TOWL plant A - totally oxidized white liquor is produced only and TOWL plant B - both types of oxidized white liquor are produced. In the operational costs, the cost of electric energy for compressors, white liquor pumps and oxygen production are included.

Table 4. Economic indicators of considered white liquor oxidation plant layouts for NaOH price of 150 EUR/t.

Parameter	POWL plant	TOWL plant A	TOWL plant B
Investment costs (mil. EUR)	1.5	3	3.5
Electricity costs (EUR/h)	5	11	23
Savings (EUR/h)	120	60	180
Profit (EUR/h)	115	49	157
Profit (mil. EUR/year)	0.98	0.42	1.33
Payback period (years)	1.5	7.1	2.6

As shown above, the best variants for installing a white liquor oxidation plant are POWL only or TOWL variant 2. Even with NaOH prices as low as 150 EUR/t the achievable profit is significant and the simple payback period, which is an indicative of a project´s feasibility, is of order of several years only.

4. Discussion

Table 3 provides an insight into composition of basic and oxidized white liquors. These differences might influence the chemicals consumption in further pulp production stages and final product quality. An experimental investigation and subsequent oxidation parameters tuning are necessary in real pulp and paper mills [16] to implement the technology successfully, without any significant disruption in production process.

Economic parameters estimated in Table 4 are extremely sensitive to NaOH price. Previous years brought significant changes in its market price, caused by unprecedented fluctuations in electricity price. Despite the volatile NaOH market price, payback periods reported in Table 4 for various plant configurations are favorable even in the low NaOH price case (150 EUR/t) adopted in calculations. Compared to simple payback periods of mid-scale projects usually acceptable by industrial companies (5 to 7 years) the investment into white liquor oxidation plant is attractive. Apart from promising project economy, the related carbon footprint reduction is another important investment impulse for any environmentally aware company. In this sense, the reported NaOH carbon footprint range [4,5] is too wide and requires a separate life cycle study to confirm the claimed environmental benefits.

Besides white liquor oxidation, other alternatives such as green- or black liquor oxidation could be considered, each having different impact on both chemicals consumption in pulping process and on paper mill's in-house steam and electricity generation. A more complex study, dedicated on techno-economic and environmental evaluation of each of those investment opportunities would contribute to the efforts to decarbonize the pulp and paper industry.

5. Conclusions

A conceptual assessment study on white liquor technology implementation in a large-scale paper mill is presented, including basic chemicals balances and chemicals saving potential identification and quantification. Financial saving and emissions reduction resulting from three white liquor oxidation plant layouts are estimated. The obtained simple payback period of 1.5 to 7 years for conservative NaOH price estimate (150 EUR/t) is promising and shows the potential of such saving measure adoption by paper mills. A further study dedicated on techno-economic and environmental comparison of available oxidation technologies applied to various stages of chemicals recovery cycle in paper mills is the next goal.

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References

1. Rajabloo, T.; De Ceunick, W.; Van Wortswinkel, L.; Rezakazemi, M.; Aminabhavi, T. Environmental management of industrial decarbonization with focus on chemical sectors: A review. *J. Environ. Manage.* **2022**, *303*, 114055.
2. Gerres, T.; Ávila J.P.Ch.; Llamas, P.L.; San Román, T.G. A review of cross-sector decarbonisation potentials in the European energy intensive industry. *J. Cleaner Prod.* **2019**, *210*, 585–601.

3. Ek, M.; Gellerstedt, G.; Henriksson, G. *Pulping Chemistry and Technology. Volume 2 Pulping Chemistry and Technology.* De Gruyter: Berlin, Germany, 2009; pp. 201–238.
4. Thannimalay, L.; Yusoff, S.; Zin Zawawi, N. Life Cycle Assessment of Sodium Hydroxide. *Aust. J. Basic Appl. Sci.* **2013**, *7*(2), 421–431.
5. Turner, L.K.; Collins, F.G. Carbon dioxide equivalent (CO_2-e) emissions: A comparison between geopolymer and OPC cement concrete. *Constr. Build. Mater.* **2013**, *43*, 125–130.
6. Valmet. White liquor oxidation system. Available online: https://www.valmet.com/pulp/cooking-and-fiberline/oxygen-delignification/white-liquor-oxidation/ (Accessed on 28 February 2023).
7. Sixta, H. *Handbook of Pulp*, 1st ed.; WILEY-VCH: Weinheim, Germany, 2006; pp. 170–191.
8. Magnotta, V.L.; Naddeo, R.C.; Ayala, V.; Cirucci, J.F.; Fox Jr., V.G. *Selective white liquor oxidation*. Air Products and Chemicals Inc, USA, United States Patent 5382322, published on 17 January 1995.
9. Alsultanny, Y.A.; Al-Shammari, N.N. Oxygen Specific Power Consumption Comparison for Air Separation Units. *Eng. J.* **2014**, *18*(2), 67–80.
10. Sanchez, D.R. Recausticizing – principles and practice. Available online: https://www.tappi.org/content/events/08kros/manuscripts/2-1.pdf (Accessed on 12 January 2023).
11. Choudhury, K.C.; Satyanarayana, U.V.; Suri, P.K. Use of Kraft White Liquor as partial replacement of Caustic in Oxygen Delignification – Lab study and plant experience. *Pap. India* **2012**, *15*(1), 24–30.
12. Perry, R.H.; Green, D.W. *Perry's Chemical Engineers' Handbook*, 7th Edition. McGraw-Hill: New York, USA, 1999; pp. 9-63–9-78.
13. Towler, G.; Sinnott, R. *Chemical Engineering Design: Principles, Practise and Economics of Plant and Process Design*. Elsevier: Oxford, UK, 2013; pp. 307-349.
14. Average monthly electricity wholesale price in Czechia from January 2019 to January 2023. Available online: https://www.statista.com/statistics/1314520/czechia-monthly-wholesale-electricity-price/ (Accessed on 20 February 2023).
15. Caustic Soda price index. Available online: https://businessanalytiq.com/procurementanalytics/index/caustic-soda-price-index/ (Accessed on 4 March 2023).
16. Khajornpaisan, N.; Rojanarowan, N. The effect of oxidized white liquor on pulp brightness in peroxide bleaching in pulp mills. *Adv. Mater. Res.* **2014**, *974*, 230-234.

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