Supporting Information

Membrane Filtration Opportunities for the Treatment of Black Liquor in the Paper and Pulp Industry

Olenka Jibaja Valderrama [1], Karina Listiarini Zedda [2] and Svetlozar Velizarov [1,*]

[1] LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade Nova de Lisboa, P-2829-516 Caparica, Portugal

[2] Water Technologies and Solutions, D-06731 Bitterfeld-Wolfen, Germany; karina.zedda@suez.com

* Correspondence: s.velizarov@fct.unl.pt; Tel.: +351-212948550

1. Equations:

The permeate flux, J_v, was calculated using Equation S1.

$$J_v = \frac{V}{A_m t} \qquad (S1)$$

Where *V* is the volume of permeate, A_m is the membrane area and t is the filtration time.

The rejection of salts based on conductivity is defines as:

$$R(\%) = \left(1 - \frac{Permeate\ conductivity}{Feed\ conductivity}\right) \times 100 \qquad (S2)$$

To calculate the transmembrane pressure (TMP), Equation S3 was considered:

$$TMP = \Delta p - \Delta\pi \qquad (S3)$$

Where Δp is the operating pressure of the system and $\Delta\pi$ is the osmotic pressure difference, which was calculated using Equation S4:

$$\Delta\pi = \pi_{feed} - \pi_{permeate} \qquad (S4)$$

The osmotic pressure of a solution with *n* components *i* used was estimated by the Van't Hoff Equation S5:

$$\pi = \sum_{i=1}^{n} C_i \times R \times T \qquad (S5)$$

Where *Ci* is the molar concentration of the component *i* in the solution (mol L^{-1}), *R* is the ideal gas constant and *T* is the temperature (K).

The amount of OH- in the feed and permeate samples was calculated using Equations S6 and S7.

$$pH = 14 - pOH \qquad (S6)$$

$$pOH = log[OH^-] \qquad (S7)$$

In Equation S8, W_{feed} is the energy required in the feed pump per m^3 of feed, *TMP* is the transmembrane pressure and η is the pump efficiency. In Equation S9, W_{recirc} is the energy required in the recirculation pump, ΔP_f is the average frictional pressure drop, *CFV* is the crossflow velocity, *D* and *L* are the diameter and length of the flow channel in the membrane and J_{av} is the average flux.

$$W_{feed} = \frac{TMP \times Q_{feed}}{\eta} \qquad (S8)$$

$$W_{recirc} = \left(\frac{\Delta P_f \times CFV \times D}{4\eta \times J_{av} \times L}\right) \qquad (S9)$$

1.1. Calculation of osmotic pressures and transmembrane pressures:

The osmotic pressure in the feed (π_{feed}) was calculated considering that the fixed temperature was 40°C. The total molar concentration was calculated from the valences and molar concentrations of each of the components of the feed (Na^+, Mg^{2+}, OH^-, SO_4^{2-} and CO_3^{2-}), giving a final value of 0.65 mol L^{-1}. As a result, the osmotic pressure was 16.91 bars:

$$\pi_{feed} = \sum_{i=1}^{n} 0.65 \times 0.0821 \times 313.15 = 16.91\ bar$$

Considering that the temperature of the permeate was 22.7 °C in average, the osmotic pressures of the permeate side for Membranes A (π_{Perm-A}), B (π_{Perm-B}) and C (π_{Perm-c}) were calculated using the compositions of the permeates obtained with each membrane. Finally, the transmembrane pressures were determined as the difference between the operating pressure (in this case, 35 bars) and the osmotic pressure difference (rounded to the decimal place) in each case. The results are summarized in Table S2.

Table S2. Transmembrane pressures (bar)

	Operating pressure (ΔP)	Osmotic pressure of the feed (π_{feed})	Osmotic pressure of the permeate (π_{perm})	Osmotic pressure difference (Δπ)	Transmembrane pressure (TMP)
Membrane A			3.42	13.5	21.5
Membrane B	35.0	16.91	1.55	15.4	19.6
Membrane C			4.58	12.3	22.7

2. Life cycle assessment:

2.1. Definition of the goal and scope

This study was complimented by a preliminary life cycle assessment to compare the environmental impact of two treatment options for black liquor: incineration through recovery boilers and a UF/NF membrane system. The data obtained could provide relevant starting information for investors, who are considering a possible implementation of one of the options. For both treatment processes, the system boundaries were defined around the process operation phase Figure S1. The construction and dismantling phases were not considered in this study.

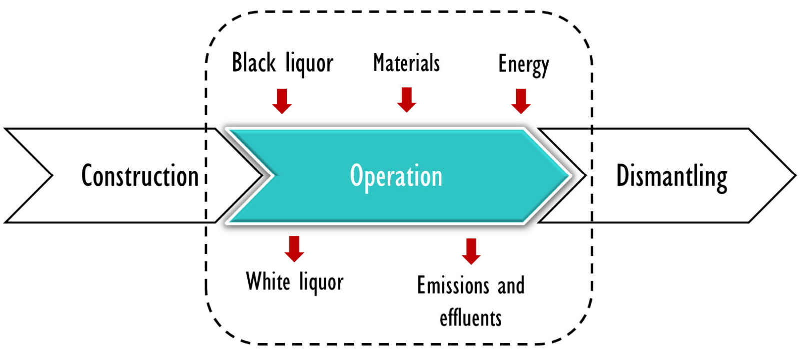

Figure S1. Goal and scope of the LCA study

Both systems had the goal to treat black liquor and recover the white liquor, so the functional unit in both cases was 1 m^3 of treated black liquor with the required characteristics to be reused in the cooking process. All the inputs and outputs of the systems were related to this functional unit.

2.2. Inventory assessment

As part of the inventory assessment, environmentally relevant data was collected in order to quantify the inputs and outputs of the two alternatives to be evaluated. For the recovery of white liquor from black liquor using recovery boilers. the main inputs of the system were the energy consumed and the chemicals. For the recovery of white liquor from black liquor using membrane technologies, the main input of the system was the energy consumed. All the material outputs were expressed as kg m^{-3} of black liquor or kg TJ^{-1} of energy generated. The energy inputs were expressed as kWh m^{-3} of black liquor. In Scenario 1, the chemical recovery required 13 kWh m^{-3} of black liquor to operate [1]. In Scenario 2, the energy consumption was 0.15 kWh m^{-3} for UF and 1.61 kWh m^{-3} for NF.

Table S3 shows the outputs using the conventional process based on the emission factors. For the membrane process. Given the small amount of cleaning solutions required for the operation of the membrane process, they were not considered in the LCA.

Table S3. Outputs using the conventional process [2]

Unit process	Output	Amount
Recovery boiler, lime combustion	CO_2	64.40 kg m^{-3} of black liquor
Energy generation	CO_2	110,000 kg TJ^{-1} of energy generated
Recovery boiler, smelt tank, lime combustion, energy generation	Particulates	24 kg m^{-3} of black liquor
Evaporator, recovery boiler, smelt tank	TRS (reduced sulfur compounds)	0.13 kg m^{-3} of black liquor
Recovery boiler, smelt tank, lime combustion	SO_2	7.80 kg m^{-3} of black liquor
Recovery boiler, smelt tank, lime combustion	NO_x	13.70 kg m^{-3} of black liquor
Energy generation	NO_x	100.00 kg TJ^{-1} of energy generated
Recovery boiler	CO	55.00 kg m^{-3} of black liquor
Energy generation	CO	4,000 kg TJ^{-1} of energy generated
Evaporation, recovery boiler	NMVOCs	3.82 kg m^{-3} of black liquor
Energy generation	NMVOCs	50 kg TJ^{-1} of energy generated
Energy generation	CH_4	30 kg TJ^{-1} of energy generated
Energy generation	N_2O	4 kg TJ^{-1} of energy generated

2.3. Calculation of emissions and environmental impacts

Five environmental categories were considered: global warming, acidification, eutrophication, smog and human toxicity. The emissions related to each of these categories are summarized in Table S4.

Table S4. Emissions in each environmental category

Environmental category	Emissions
Global warming	CO_2, CH_4 and NO_x
Acidification	SO_2 and NO_x
Eutrophication	NO_3^-, PO_4^{3-}, total N and total P.
Smog	NMVOC, CO, CH_4, NO_x
Human toxicity	Particulates, AOX, TRS, SO_2 and NO_x

The total emissions are calculated using Equation S10:

$$Total\ of\ Emissions = Activity \times Emission\ factor \qquad (S10)$$

In the scope of this study, the activities in the black liquor treatment that contribute to the emissions included the chemical recovery unit and the energy generation unit. These activities were related to the production capacity of the plant. For each of the 2 options in evaluation, the capacity of the system was considered as stated in Table S5.

Table S5. Activity data in the chemical recovery unit for the calculation of the emissions

Activity	Scenario 1	Scenario 2
Conventional process	150 m^3 of black liquor per hour	135 m^3 of black liquor per hour
Membrane process	0 m^3 of black liquor per hour	15 m^3 of black liquor per hour
TOTAL	150 m^3 of black liquor per hour	150 m^3 of black liquor per hour

For the calculation of the amount of energy generated using the conventional process, it was assumed that 1,500 tons of black liquor solids could generate 30 MW of energy and that 10 tons of black liquor had 1.50 of dry solids [3]. The total energy generated would be 13.20 x 10^{-3} TJ h^{-1} in Scenario 1 and 11.88 x 10^{-3} TJ h^{-1} in Scenario 2.

The emission factors for each process under evaluation are detailed in Tables S6 and S7. Table S6 refers to the processes involved in the chemical recovery and Table S7 to the energy generation. Since this evaluation took into account the implementation of the proposal in Sweden, the emissions of energy generation correspond to the use of biomass as it is one of the main energy sources in Sweden.

Table S6. Emission factors in the chemical recovery unit from Kraft pulp production

Process	Output	Amount (kg m^{-3} of black liquor)	Source
Evaporation	NMVOCs	0.520	[4]
	TRS	0.010	[5]
Recovery boiler	CO_2	61.800	[6]
	SO_2	2.060	[5]
	NO_x	10.610	[7]
	CO	56.650	[7]
	NMVOCs	3.420	[7]
	TRS	0.030	[5]
	Particulates	12.360	[5]
Smelt tank	SO_2	0.310	[5]
	NO_x	0.100	[5]
	TRS	0.090	[5]
	Particulates	1.030	[5]
Lime combustion	CO_2	4.530	[8]
	SO_2	5.665	[5]
	NO_x	3.399	[5]
	Particulates	1.030	[9]

Table S7. Emission factors in the energy generation unit from Kraft pulp production

Process	Output	Amount	Units	Source
Energy generation unit	CO_2	110	ton TJ^{-1}	[9]
	CH_4	0.030	ton TJ^{-1}	[9]
	N_2O	0.004	ton TJ^{-1}	[9]
	NMVOC	0.050	ton TJ^{-1}	[9]
	CO	4	ton TJ^{-1}	[9]

	NO_x	0.100	ton TJ^{-1}	[9]
	Particulates	10.300	kg m^{-3} of black liquor	[4]

The next step was the calculation of the environmental impacts, which was determined using Equation S11:

$$Impact = Total\ emissions \times Classification\ factor \qquad (S11)$$

In the classification, the inventory inputs and outputs were assigned to the selected environmental categories. The classification factors for the 5 environmental categories evaluated in this study are presented in Table S8.

Table S8. Classification factors used for emissions for 1 kg of pollutants

Environmental category	Compound	Classification factor	Reference
Global warming	CO_2	1 CO_2-eq	[9]
	CH_4	21 CO_2-eq	
	N_2O	310 CO_2-eq	
Acidification	SO_2	1 SO_2-eq	[10]
	NO_x	0.710 SO_2-eq	
Eutrophication	NO_x	0.130 PO_4-eq	[10]
Smog	NMPOC	0.416 ethylene-eq	[10]
	CO	0.027 ethylene-eq	
	CH_4	0.006 ethylene-eq	
	NO_x	0.028 ethylene-eq	
Human toxicity	TRS	0.220 $C_6H_4Cl_2$-eq	[10]
	SO_2	0.096 $C_6H_4Cl_2$-eq	
	NO_x	1.200 $C_6H_4Cl_2$-eq	
	Particulates	0.820 $C_6H_4Cl_2$-eq	

In this part of the study, the information in the inventory table was related to the impact categories and indicators in order to analyze the environmental impacts of each of the scenarios for the recovery of white liquor. The environmental categories considered were global warming, acidification, eutrophication, smog formation and human toxicity.

2.4. Impact assessment results

As illustrated in Figure S2, the treatment process that had the higher contribution in the different impact categories analyzed for the two scenarios was the recovery boiler. After an individual analysis of each environmental category, a comparison between the two options was made. A summary of the total environmental impacts is shown in Table S9.

Table S9. Comparison between the impact assessment results for Scenario 1 and Scenario 2

Impact category	Unit	Scenario 1	Scenario 2	Decrease
Global warming	ton CO_2-eq h^{-1}	10,735.13	9,665.76	9.96%
Acidification	ton SO_2-eq h^{-1}	2,708.42	2,437.58	10.00%
Eutrophication	ton ethylene-eq h^{-}	275.26	247.73	10.00%
Smog	ton PO_4-eq h^{-1}	535.14	481.72	9.98%
Human toxicity	ton $C_6H_4Cl_2$-eq h^{-1}	5,701.49	5,258.11	7.78%

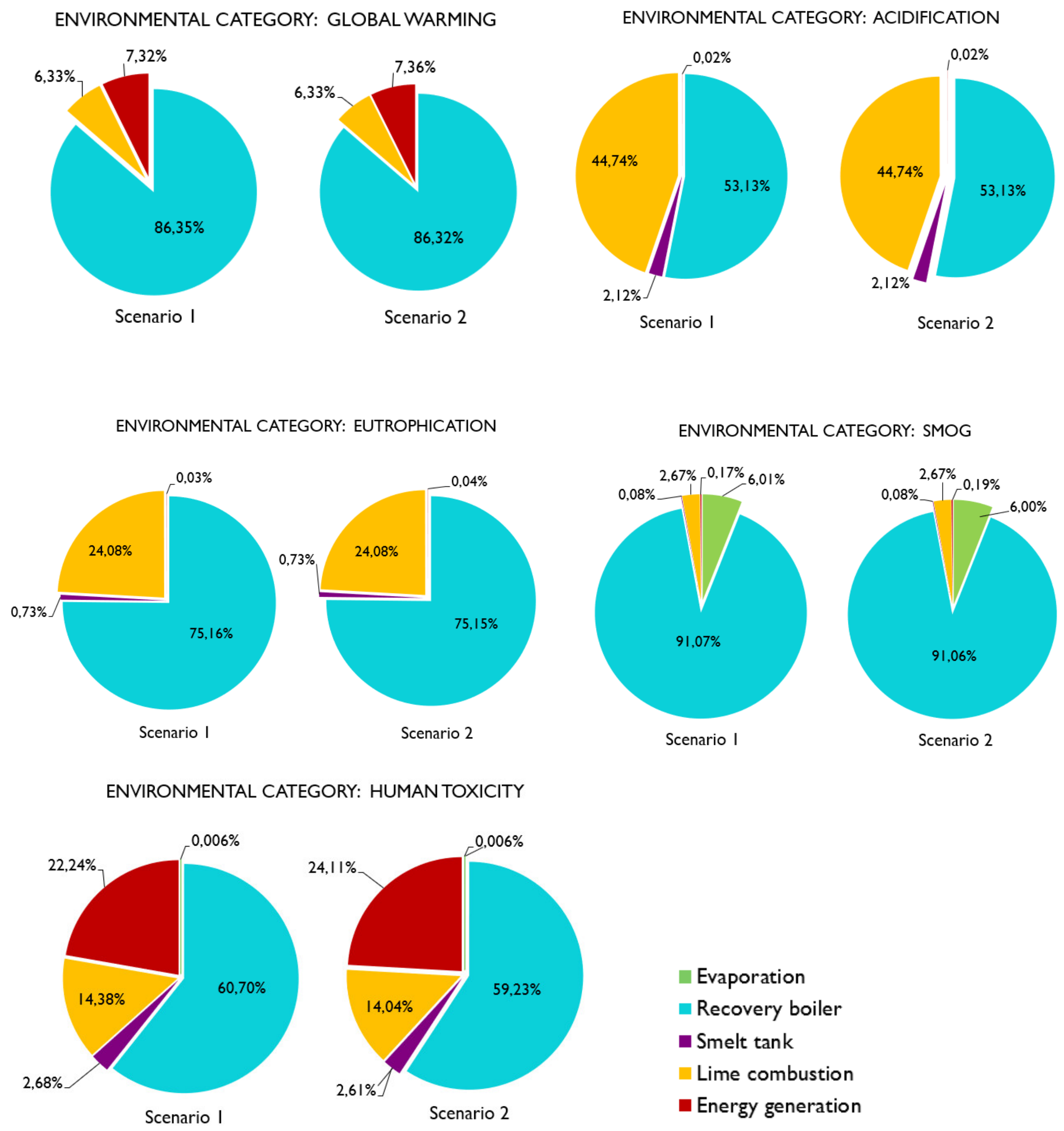

Figure S2. Impact assessment results

Abbreviations:

(Abbreviations are listed alphabetically)

AOX	Adsorbable Organic Halides
EDTA	Ethylenediaminetetraacetic acid
GWP	Global Warming Potential
LCA	Life cycle assessment

NF	Nanofiltration
NMVOC	Non-methane volatile organic compounds
TMP	Transmembrane pressure
TRS	Total Reduced Sulphur
VOC	Volatile organic compounds

References:

1. (CAR/PL), C.d.A.R.p.l.P.L. *Prevención de la contaminación en el sector papelero*; Spain, 2005.
2. Loutfi, H.; Blackwell, B.; Uloth, V. Lignin recovery from kraft black liquor: Preliminary process design. *Tappi Journal* **1991**, *74*, 203-210.
3. Wallberg, O.; Jönsson, A.-S. Separation of lignin in kraft cooking liquor from a continuous digester by ultrafiltration at temperatures above 100°c. *Desalination* **2006**, *195*, 187-200.
4. JRC, D.-G. Integrated pollution prevention and control (ippc) reference document on the application of best available techniques to industrial cooling systems. **2001**.
5. Bordado, J.C.M.; Gomes, J.F.P. Emission and odour control in kraft pulp mills. *J Clean Prod* **2003**, *11*, 797-801.
6. Institute, T.E. *Industrial environmental performance indicators*; Thailand, 1999.
7. CORINAIR. *Atmospheric emission inventory guidebook*; European Environment Agency: Copenhagen, Denmark, 2000.
8. Association, T.P.a.P.I. *Application of the production performance indicators in accordance with global reporting initiative (gri) to thai pulp and paper industries*; Bangkok, Thailand, 2002.
9. Poyry, J. *Technical and economical evaluation of water pollution control in pulp mill*; Helsinki, Finland, 1992.
10. Jawjit, W. An environmental systems analysis of the kraft pulp industry in thailand. **2006**.