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ENVIRONMENTAL SYSTEMS ANALYSIS OF ALTERNATIVE BLEACHING SEQUENCES WITH FOCUS ON CARBON FOOTPRINT

Pia Jour[1], Karin Halldén[2] and Eva Wackerberg[1]

[1] *AkzoNobel Pulp and Performance Chemicals AB, Bohus, Sweden*
[2] *AkzoNobel AB, Gothenburg, Sweden*

ABSTRACT

Substantial efforts have been made in order to improve the environmental impact caused by kraft pulp bleaching. The shift from chlorine bleaching to elemental chlorine-free (ECF) bleaching technology has resulted in significant improvements. The development of environmental systems analysis has made it possible to widen the perspective. The whole value chain can be included and the contributions to many types of environmental effects can be quantified. The AkzoNobel experience is that Life Cycle Assessment (LCA) is a powerful method to support process and product development in order to avoid sub-optimizations. Climate change is an important environmental effect and carbon footprints are currently in focus. This paper presents an LCA of bleached eucalyptus kraft pulp production in Brazil. The system investigated includes the whole production system starting with forestry and ending with bleached pulp at the gate of the pulp mill. Alternative bleaching sequences have been compared for two different scenarios: (1) Chemical Island (an AkzoNobel concept), reflecting Brazilian conditions; and (2) Ecoinvent, representing generic LCA data for bleaching chemicals. The bleaching sequences studied are three somewhat different ECF sequences, one of them including ozone.
The main difference between the two scenarios investigated is the magnitude of the carbon footprint contribution from bleaching: for the Chemical Island scenario the contribution is 15-17% of the total carbon footprint; and for the Ecoinvent scenario the corresponding share is 34-41%. The alternative bleaching sequences studied result in rather similar carbon footprints of the bleached pulp.
There is a large span in carbon footprints of the chemicals used for pulp bleaching. It is crucial to select data sets that are relevant in terms of geography and technology. The most dominant contributors to the carbon footprint of the unbleached pulp are forestry and pulp production. Although focus has been on carbon footprint, the contributions to other environmental effects commonly included in LCAs (ozone depletion, acidification, eutrophication and photochemical ozone formation) have also been assessed and only minor differences between the alternative bleaching sequences were found. The results presented in this study have been reviewed by experts in LCA of pulp and paper at the Technical Research Centre of Finland (VTT).
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Keywords: *Life cycle assessment (LCA), carbon footprint, eucalyptus kraft pulp production, Brazil, elemental chlorine-free (ECF) bleaching, Chemical Island*

1. INTRODUCTION

Substantial improvements have been made in recent decades when it comes to kraft pulp bleaching; the environmental impact per ton of bleached pulp caused by bleaching has been significantly reduced. Thirty years ago molecular chlorine was commonly used for pulp bleaching. Nowadays, elemental chlorine-free (ECF) bleaching, using chlorine dioxide (ClO_2), is the dominating technology, having a market share of 87% of the bleached kraft pulp capacity worldwide (Fisher Solve 2011). Total elemental chlorine-free (TCF) bleaching has a market share of only 3% and about 10% of the bleached kraft pulp is still bleached using chlorine or hypo chlorite. Around 7% of the bleached kraft pulp is produced by using an ECF or TCF bleaching sequence including ozone.

A number of Life Cycle Assessments (LCAs) comparing alternative bleaching sequences have been published (Hostachy 2010; Métais and Hostachy 2011; Ryynänen and Nelson 1996; and Zhi Fu *et al*. 2005). While Ryynänen and Nelson (1996) concluded that the difference in environmental performance between ECF and TCF bleached pulp is minor, Hostachy (2010) and Métais and Hostachy (2011) conclude that ozone bleaching is significantly better than

Corresponding author: *Pia Jour. AkzoNobel. Bohus. SE-445 80. Sweden. Phone: +46 31 58 70 94. pia.jour@akzonobel.com.*

conventional ECF bleaching in terms of environmental performance. According to published LCAs of pulp and paper products, the relative significance of the bleaching (i.e., the bleaching process at the pulp mill and production of bleaching chemicals) vary depending on the type of environmental impact (González-Garcia *et al.,* 2009b; and Jawjit *et al*., 2006).

AkzoNobel Pulp and Performance Chemicals (former Eka Chemicals) is using LCA to evaluate the environmental performance of its products in order to support product and process development. Over the years an extensive LCA database for our products and processes has been built. On a company level, the emissions of greenhouse gases (the carbon footprint) are annually monitored and targets for reduction are set.

The purpose of this study is to use LCA to quantify and compare the environmental impact of ECF bleaching sequences with and without ozone present. Although focus is on the environmental effect climate change (measured as carbon footprint), other types of environmental effects (e.g. eutrophication) have been included in the analysis. Knowledge of what type of environmental impact and the magnitude caused by the different parts of the pulp making value chain is valuable when striving towards minimization of the negative environmental impact caused by pulp production. This is why not only the alternative bleaching processes have been assessed and compared, but the whole pulp production systems starting with forestry and ending with the bleached pulp ready for distribution at the pulp mill gate. The study to be described in this paper has been critically reviewed by experts in LCA of pulp and paper at the Technical Research Centre of Finland (VTT).

2. METHODS

The method used is the systems analysis method, Life Cycle Assessment (LCA), performed according to the ISO standards 14040 (2006) and 14044 (2006) and, as far as possible, in line with the requirements of the ISO standard on the carbon footprint of products currently in preparation (ISO/DIS 14067.2). The LCA method emerged in the 1960s and during the 1990s the evolution was rapid. LCA is a method to analyze and assess the environmental impact of a product or service throughout its entire life cycle. A complete life cycle includes raw material extraction, processing, transportation, packaging, storage, use and waste management, see Figure 1. The flows of energy and material into and out from the system studied are accounted for. These flows (often called inputs and outputs) of different systems can be compared directly; however the parameters are often numerous, which makes interpretation difficult. Aggregation of data is therefore carried out to facilitate interpretation. The contribution to various environmental effects (e.g. climate change) can be assessed. Another option is to carry out a valuation procedure and calculate a single performance index.

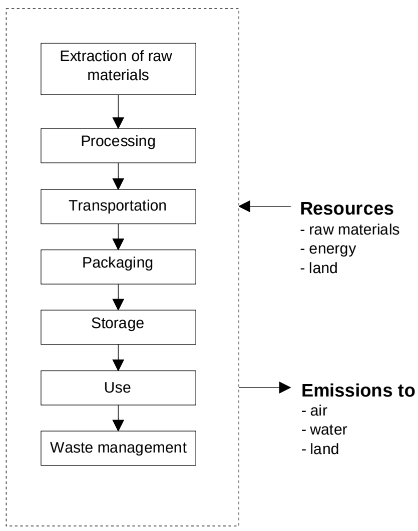


Figure 1: Overall scheme of a product's life cycle.

Life Cycle Assessments are intended to support decisions; the decision makers may be authorities, companies or consumers. Comparative studies are common, for example, products with the same function, different process alternatives or different waste handling alternatives can be compared. However LCA can also be used for individual products with the aim to identify opportunities for environmental improvements. For this, comparisons are made between the different parts of the life cycle. The following are examples of how LCAs have been used by authorities and companies:

- to support legislation and public policy making;
- to improve the environmental performance of products / product development;
- to choose between raw materials and suppliers;
- to make market claims; and
- as input to strategic planning.

A getting started guide for LCA can be found at the tosca website (EU Life project "Towards sustainable supply chains through a common approach for company strategic work and daily operations", www.tosca-life.info).

The present study was carried out by using a commercial LCA software (GaBi 4, PE International) and the methodology used is described in sections 2.1 – 2.5 below**.** Further this study has been critically reviewed by VTT to ensure that the methods used to carry out the LCA are consistent with ISO 14040 and ISO 14044. Other goals with the review by VTT were: to get feedback on the study versus the requirements of the ISO standard on the carbon footprint of products currently in preparation (ISO/DIS 14067.2); to ensure that the data used are appropriate and reasonable in relation to the goal of the study; and finally, to ensure that the interpretations reflect the limitations identified and the goal of the study.

2.1 Goal and scope

The goal of the study is to compare the environmental performance, with focus on the carbon footprint, of an eucalyptus kraft pulp bleached in the following alternative ways:
1) ECF, state of the art, D_{hot} (EPO) D D
2) ECF light, state of the art, D_{hot} (EPO) D P
3) ECF, average, D_{hot} (EPO) D D
4) ECF ozone, a Ze D P

Two scenarios have been studied in order to investigate the consequences of using different data sets for the bleaching chemicals.

a) **Chemical Island scenario:** Sodium chlorate produced on-site at the pulp mill in a Chemical Island, which is an AkzoNobel state-of-the-art chemicals production, management and supply concept. A benefit with this concept is that sodium chlorate can be produced using biomass energy and that less transportation is needed.
b) **Ecoinvent scenario:** Carbon footprint data sets for the chemicals chlorine dioxide (with sodium chlorate upstream), hydrogen peroxide and sodium hydroxide were collected from the Ecoinvent database. Ecoinvent is a public LCA database commonly included in commercial LCA software.

Scenario a) describes modern technology and the situation in Brazil to the best of our knowledge. Scenario b) is to be regarded as a sensitivity analysis.

The study has been conducted with focus on the environmental effect climate change. The contributions to climate change or the carbon footprint are calculated by adding up the contributions made by the various greenhouse gases such as carbon dioxide, nitrous oxide and methane, with the unit kg CO_2-equivalents. The carbon footprint calculations carried out in this study exclude the biogenic emissions of carbon dioxide. This means that neither the carbon dioxide sequestered by the growing eucalyptus trees, nor the release of the sequestered carbon dioxide back to the atmosphere have been accounted for. Part of the biogenic carbon is released when steam and electricity is produced from biomass in the pulp mill. Part of the biogenic carbon leaves the pulp mill with the pulp and is released in the waste management of the final product produced from the pulp. This delimitation was made since the uptake is the same as the release, even though there is a difference in time.

The contributions to several environmental effects have been assessed in order to find out if there are significant differences between the bleaching sequences investigated. The environmental impact categories included in this study and the method used to aggregate the quantified inputs and outputs are as follows:

- **climate change** (Solomon *et al*. 2007);
- ozone depletion (IEC 2008);
- acidification (IEC 2008);
- eutrophication (IEC 2008);
- photochemical ozone formation (IEC 2008); and
- primary energy use, renewable and non-renewable (IEC 2008).

The impact category, climate change, was selected since it is an important global environmental effect modelled well by LCA. The other environmental effects were selected since they are commonly included in AkzoNobel LCAs, Environmental Product Declarations (EPDs, www.environdec.com), and eco-footprint leaflets (data and information from LCAs compiled in leaflets for communication with customers). They are modelled well by LCA, even though some of them are not global but regional or local environmental effects (acidification, eutrophication and photo-oxidant formation).

2.2 System boundary

The system boundary is very important in systems analysis. If a comparison is going to be made, it is necessary to make sure that the systems compared are delivering the same products and/or services. Two terms referring to system boundaries are commonly used in LCAs: cradle-to-gate and cradle-to-grave. Cradle-to-gate means that the system boundary starts with extraction of natural resources from nature and ends with a product ready for distribution at the gate of the production site. Cradle-to-grave means that the processes after the production of the product also have been included, e.g. transport to the mill, and use of the pulp at the paper mill, distribution of the paper product to the print house, printing of magazine, distribution of magazines, use and final waste management such as recycling, waste incineration and/or landfill.

Cradle-to-gate results are suitable for communicating with customers. This is the system boundary typically used in EPDs and ecofootprint leaflets in order to allow the customer to carry out an LCA or carbon footprint calculation for his or her product.

The study reported here is a cradle-to-gate LCA and the system boundaries are explained in detail in Figure 2. Forestry and manufacturing of unbleached pulp is included in order to understand the relative significance of bleaching. The eucalyptus plantations and the pulp mill are located in Brazil. Bleaching and manufacturing of bleaching chemicals has been studied in more detail. In this case, the Chemical Island scenario means that not only chlorine dioxide but also sodium chlorate is produced at the pulp mill site. Thus, the production of sodium chlorate can benefit from access to steam and electricity produced from biomass. The Ecoinvent scenario, on the contrary, assumes sodium chlorate to be produced in a separate production unit and that there is a transport by lorry and train to the on-site chlorine dioxide generator. The Ecoinvent data for sodium chlorate is based on information from European manufacturers. It is important to note that the electricity used for production of both sodium chlorate and chlorine dioxide in the Ecoinvent calculations is an European electricity mix called UCTE – Union for the Coordination of the Transmission of Electricity (with a high percentage of fossil based power).

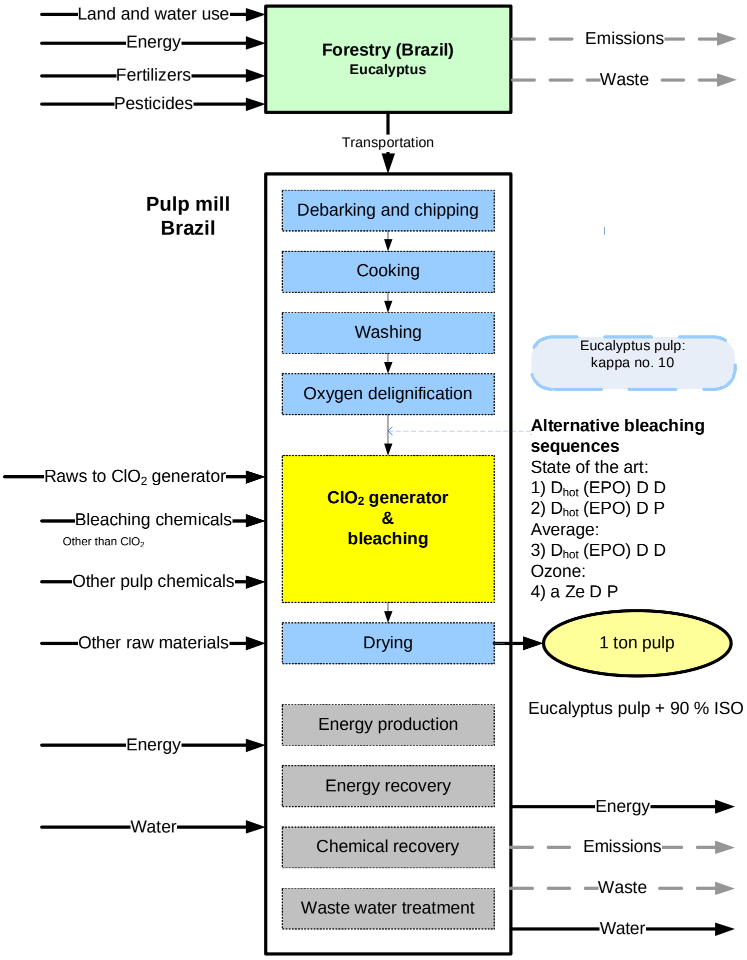


Figure 2: The system studied. In the Chemical Island scenario, the sodium chlorate plant is also located at the pulp mill site.

2.3 Functional unit

Another important term in LCA is the so-called functional unit, which is the basis for the comparison. It is often defined as one ton of product, and in the study presented here, the functional unit is one ton of bleached pulp at the gate of the pulp mill in Brazil.

2.4 Data collection

When carrying out an LCA, a lot of information and data is needed. The relevance and quality of the data used will influence the validity of the results. This is why a critical review also includes a careful control of the data used to be appropriate and reasonable for the goal of the study. The type of data used for the different parts of the value chain is described below.

1. Public/published data has been used to model:
    a. Forestry and eucalyptus plantations in Brazil (Aracruz Celulose 2003; Aracruz Celulose 2008; Gonzáles-García *et al*. 2009a; and Jawjit *et al.* 2006)
    b. Energy production (Brännström-Norberg *et al*. 1996; Ecoinvent ver 2.2*)*
    c. Transportation (PE International – GaBi 4; NTM 2008)
2. A mix of published and internal data has been used to model:
    a. Production of unbleached pulp (IPPC 2001; IFC, 2006)
    b. Pulp bleaching (AkzoNobel 2012*,* Hostachy 2010)
    c. Production of chemicals (Ecoinvent ver 2.2, PE International – GaBi 4, AkzoNobel 2012)
3. Site specific data is data that has been collected by using data collection questionnaires asking for all the inputs and outputs of the process from the production site in question. Site-specific data has been used to model the bleaching chemicals chlorine dioxide, sodium chlorate and hydrogen peroxide produced by AkzoNobel.

The alternative bleaching sequences and their charges of chemicals are presented in Table 1. For the two state of the art bleaching sequences, ECF and ECF light, the charges are representative for a modern mill. For ECF average, the charges have been calculated based on the average consumption of chlorate for eucalyptus pulp bleaching in Brazil (AkzoNobel) For ECF ozone, the same charges as applied by Hostachy (2010) have been used.

Further, the energy balance of a generic pulp mill in Brazil has been used as the source of information with regards to the use of both wood and different energy carriers (*Source: Jaakko Pöyry*).

Table 1. The charge of chemicals (kg/t pulp), as 100%, used in the calculations for the different sequences. Note that for sulphuric acid, the concentration is 96%.

	Chemical charges (kg/t pulp)			
Chemicals	ECF ozone(1) aZeDP	ECF average D_{hot}(EPO)DD	ECF state of the art D_{hot}(EPO)DD	ECF light state of the art D_{hot}(EPO)DP
Chlorine dioxide	8	14.8	9.9	7.6
Chlorine dioxide as aCl	21	39	26	20
Hydrogen peroxide	5	2	2	6
Oxygen	0	3	3	3
Sodium hydroxide	12	12	12	14
Sulphuric acid	18	6	6	6
Ozone	5	0	0	0

(1) Literature data from Hostachy (2010)

2.5 Key assumptions

When carrying out an LCA it is necessary to make assumptions. The most important assumptions used in this study are the following:

- The pulp is produced in a kraft process.
- The chlorine dioxide is produced in a generator of the type Single Vessel Process - Salt Cake Wash, SVP-SCW (AkzoNobel Pulp and Performance Chemicals, http://www.akzonobel.com/eka).
- In the Chemical Island scenario the steam and electricity required for the ClO_2 generator is produced from biomass (part of the pulp mill excess energy).
- The remaining pulp mill excess electricity can be exported to the national electricity grid in Brazil and replaces the production of an average Brazilian electricity mix.
- The oxygen and ozone used in the bleaching process is produced on-site with electricity produced from biomass (part of the pulp mill excess energy).

3. RESULTS AND DISCUSSION

This section will start with an analysis of the unbleached kraft pulp and the consequences for the carbon footprint due to the varying amounts of pulp mill excess electricity available for export to the national grid. Next is an analysis of the carbon footprint data for the chemicals used in the bleach plant and of the contributions from the different parts of the value chain for both unbleached and bleached pulp. The carbon footprint is analysed with respect to the different greenhouse gases and their contributions. Finally, other environmental effects are also assessed.

3.1 Export of pulp mill excess electricity

In this study we have assumed that the mill is connected to the national grid making it possible to export the excess electricity. However, this is not an option for all mills in Brazil today. The amount of pulp mill excess electricity available for export will vary between the scenarios. This will influence the outcome of the LCA, e.g. carbon footprints of the unbleached pulp. Table 2 shows the amounts of excess electricity as well as the carbon footprints for unbleached eucalyptus pulp (including forestry, transport of wood, pulping chemicals and production of unbleached pulp) produced in Brazil. According to our calculations, the carbon footprint can vary between 181 and 202 kg CO_2-equivalents per ton of unbleached pulp.

For a pulp mill without a Chemical Island and/or on-site ozone production, 100% of the excess electricity can be exported to the national grid. In this case, the amount of excess electricity is 1627 MJ per ton of unbleached pulp. The excess electricity is assumed to replace electricity production corresponding to the average Brazilian national grid mix. Since this means an avoidance of electricity production elsewhere, the carbon footprint of the unbleached pulp will be somewhat lower compared to a case where electricity export is not possible. As shown in Table 2, the resulting carbon footprint in this case is 181 kg CO_2-equivalents per ton of unbleached pulp.

With a Chemical Island at the pulp mill site, a part of the excess electricity is used to produce sodium chlorate. Thus, there will be less excess electricity to export from the pulp mill to the national grid, resulting in a higher carbon footprint (191 kg CO_2-equivalents per ton of unbleached pulp). This drawback is well compensated for when looking at the total carbon footprint of the bleached pulp, due to the benefit of having access to sodium chlorate/chlorine dioxide with a low carbon footprint. In this case, the assumption is that all of the sodium chlorate produced is consumed on-site in the chlorine dioxide generator, i.e., no production of excess chlorate for export to other pulp mills in the region. To calculate the amount of electricity required by the sodium chlorate production, an average consumption of 11.2 kg ClO_2 per ton of bleached pulp was used (median value for the four bleaching sequences, see Table 1); 1.63 kg sodium chlorate per kg ClO_2 and 19.6 MJ electricity per kg chlorate.

When the pulp mill uses ECF ozone bleaching, a part of the excess electricity is needed for the production of ozone. On-site production of ozone from oxygen requires 386 MJ electricity per ton of pulp when a charge of 5 kg ozone per ton of pulp is used. Thus, there will be less excess electricity to export from the pulp mill to the national grid. This is why the carbon footprint per ton unbleached pulp is higher in the scenarios involving ozone bleaching (192 kg CO_2-equivalents per ton of unbleached pulp). If the scenarios involve both ozone bleaching and a Chemical Island, the carbon footprint will be even higher; 202 kg CO_2-equivalents per ton of unbleached pulp.

Table 2. Excess electricity and carbon footprint for unbleached eucalyptus pulp produced in Brazil.

	Excess electricity (MJ/ton pulp)	Carbon footprint (kg CO_2/ton pulp)
No export of excess electricity	-	226
100% export of excess electricity	1627	181
Chemical Island	1270	191
Ozone bleaching	1241	192
Ozone bleaching & Chemical Island	884	202

3.2 Carbon footprint data for the chemicals used in the bleach plant

The carbon footprints of the chemicals as used in the different scenarios are presented in Table 3 below. As can be seen in the table, there is a large difference in the data for chlorine dioxide, hydrogen peroxide and sodium hydroxide between the Chemical Island and the Ecoinvent scenarios. The data used in the Chemical Island scenario is representative for AkzoNobel production units. However, the data found for these chemicals in the Ecoinvent database is much higher. For chlorine dioxide, the main reason for the difference is the electricity mix used in the production of sodium chlorate. The Ecoinvent data is representative for European manufacturers and assumes an European electricity mix, UCTE, with a quite large share of fossil energy carriers. The Chemical Island scenario means that the electricity needed for sodium chlorate production is produced from biomass. The minimum and maximum levels of data on hand for these chemicals are also shown in Table 3.

Table 3. Carbon footprint (kg CO_2-equivalents per kg chemical) for the chemicals used in the bleach plant and the span, minimum and maximum, between data from different databases on hand.

Chemical (conc. %)	Chemical Island scenario	Ecoinvent scenario	Minimum in databases	Maximum in databases
Chlorine dioxide (100%)	0.84(1)	6.2(3)	0.84(1)	6.2(3)
Hydrogen peroxide (70%)	0.42(4)	1.6(3)	0.38(1)	3.7(2)
Ozone	0.28(5)	0.28(5)	0.28(5)	8(3)
Sodium hydroxide (100%)	1.4(2)	2.0(3)	1.4(2)	2.5(3)
Sulphuric acid (96%)	0.24(2)	0.24(2)	0.14(3)	0.24(2)

(1) AkzoNobel (2012); (2) PE International (GaBi 4); (3) Ecoinvent (ver 2.2); (4) AkzoNobel (2012) with modified data using Brazilian electricity mix; (5) Ecoinvent (ver 2.2) with modified data using electricity produced from biomass.

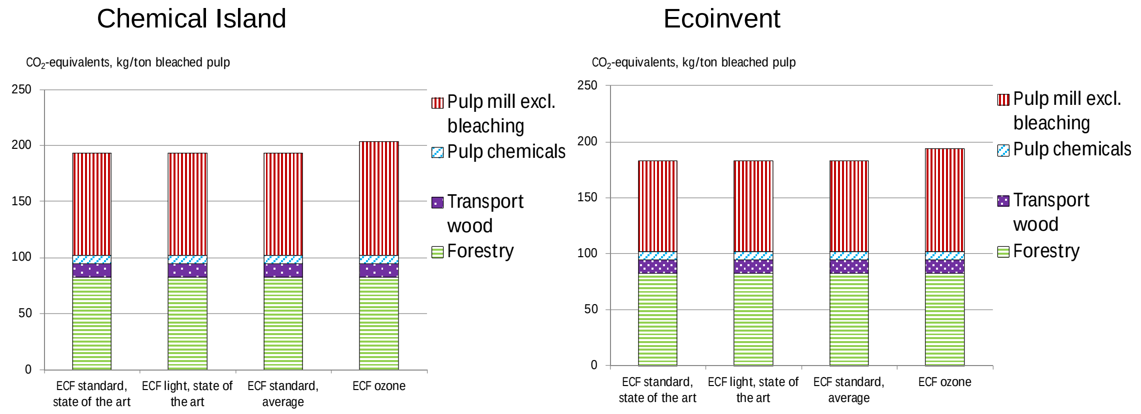
3.3 Carbon footprint of the unbleached pulp

The sum of the contributions from forestry, transportation of wood to pulp mill, pulping chemicals and the pulp mill excluding bleaching is defined as production of unbleached pulp cradle-to-gate and has been modelled in the same way for the different bleaching sequences and scenarios in this study with one exception; the amount of pulp mill excess electricity available for export (see 3.1).

Figures 3a and 3b show the carbon footprint contribution from the different parts of the value chain, from forestry to unbleached pulp for the Chemical Island and the Ecoinvent scenarios. As mentioned above, the carbon footprint of the unbleached pulp is also influenced by the different set ups in the bleach plant. For the Chemical Island scenario (Figure 3a), the contribution from the unbleached pulp for the different bleaching sequences varies between 193 (ECF, state of the art) and 204 (ECF ozone) kg CO_2-equivalents per ton of bleached pulp (1.01 ton of unbleached pulp per ton of bleached pulp).The corresponding numbers for the Ecoinvent scenario (Figure 3b) are 183 to 194 kg CO_2-equivalents per ton of bleached pulp. The somewhat lower contributions made by the unbleached pulp in the Ecoinvent scenario is explained by the amount of excess electricity available for export. The consequences of producing sodium chlorate/chlorine dioxide not using the pulp mill excess energy will show when adding the contribution made by bleaching, see section 3.4.

The carbon footprint contribution made by the pulp mill (excluding bleaching) is due to production of steam and electricity. To generate energy, not only biomass, but also a small amount of fossil energy is needed, mainly for the lime kiln (366 kWh per ton of pulp, Jaakko Pöyry). In a Chemical Island scenario it is possible to use hydrogen from the chlorate plant to replace the fossil fuel; however that has not been the case in this study. In the calculations it is assumed that the fossil fuel is natural gas.

In summary, the carbon footprint of unbleached pulp is roughly made up by 43-45% from forestry, 44-47% from the pulp mill excluding bleaching, 6-7% transport of wood and 4% from production of pulping chemicals cradle-to-gate. Even though the share of fossil energy used by the pulp mill is low, the resulting contribution to the carbon footprint is significant. Thus, ways to reduce the amount of fossil energy needed would improve the carbon footprint of the kraft pulp production.



Figures 3a and 3b: Contributions from the different parts of the value chain: forestry, transportation of wood, production of pulping chemicals and production of unbleached pulp to the total carbon footprint for the Chemical Island (a) and the Ecoinvent (b) scenarios.

3.4 Carbon footprint of the bleached pulp

Figure 4 shows the total carbon footprints per ton of bleached pulp for the two scenarios studied and also includes the contribution from bleaching and the production of bleaching chemicals. The contributions from the unbleached pulp are the same as those shown in Figures 3a and 3b. In the Chemical Island scenario, the sodium chlorate is produced on-site at the pulp mill using biomass for power, while in the Ecoinvent scenario, carbon footprint data from the public LCA database Ecoinvent has been used for the chemicals chlorine dioxide (with sodium chlorate upstream), hydrogen peroxide and sodium hydroxide. The top segment of the bars represent the contribution made by bleaching, including production of bleaching chemicals cradle-to-gate, transportation to the pulp mill and contributions from the bleaching process itself.

State of the art ECF bleaching gives the smallest carbon footprint in both scenarios, see Figure 4. ECF ozone and ECF average give the largest carbon footprint in the Chemical Island and Ecoinvent scenarios, respectively. The share of the total carbon footprint (bleached pulp) coming from bleaching is about 15-17% for the Chemical Island scenario and between 34-41% in the Ecoinvent scenario. The difference between the bleaching sequences will be analysed in more detail in Section 3.5.

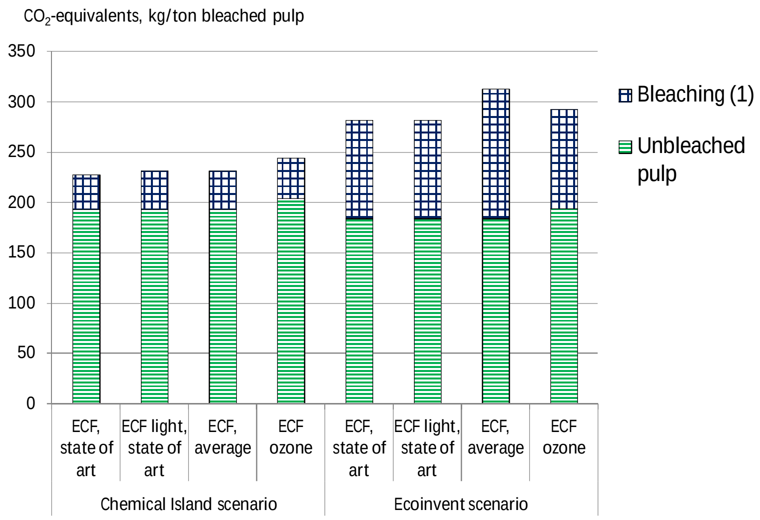


Figure 4: Carbon footprint divided between production of unbleached pulp and bleaching.
(1) Including both the bleaching process and production of bleaching chemicals cradle-to-gate.

3.5 Carbon footprint of the bleach plant in more detail

In Figure 5, the carbon footprint contribution from bleaching is further divided between the different chemicals used in the bleach plant, transportation of chemicals to the pulp mill and energy used in the bleaching process. Overall, it can be seen that the carbon footprint contributions made by bleaching are very similar; between 36 and 41 kg CO_2-equivalents per ton of bleached pulp for all sequences in the Chemical Island scenario. The bleaching sequence, ECF state of the art, is the best alternative, while the worst, ECF ozone, is only 7% higher.

In the Ecoinvent scenario, the contribution from bleaching is much higher; between 97 and 125 kg CO_2-equivalents per ton of bleached pulp. ECF state of the art, ECF light and ECF ozone are all about the same, while ECF average is the worst alternative due to the extreme carbon footprint data for chlorine dioxide in the Ecoinvent scenario and the relatively high use of chlorine dioxide.

It can also be seen that for all bleaching sequences, sodium hydroxide and chlorine dioxide contribute the most. The chlorine dioxide part also includes the production of sulphuric acid, methanol, sodium chlorate and transportation, if needed, to the ClO_2 generator. Hydrogen peroxide gives the third largest contribution to the carbon footprint in the ECF light and ECF ozone sequences due to the higher charges used in these sequences. For the ECF ozone sequence, a higher charge of sulphuric acid is used, thus a higher carbon footprint contribution is noticed.

Transportation includes transport of all chemicals not produced on-site to the pulp mill. The carbon footprint contribution due to transportation of bleaching chemicals to the pulp mill is clearly visible, but relatively small.

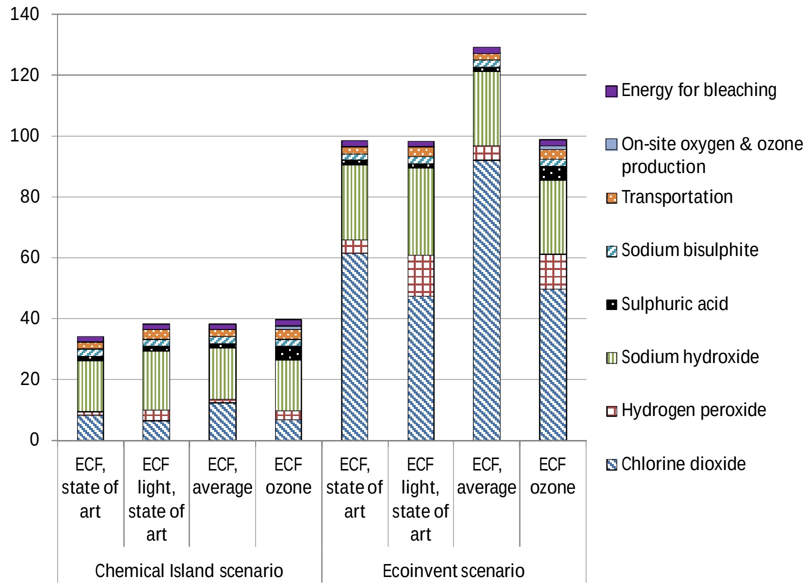


Figure 5: Carbon footprint contributions from bleaching and the production of the different chemicals used for bleaching cradle-to-gate.

3.6 The contributing greenhouse gases

Carbon footprint is not only the amount of carbon dioxide but the sum of the contributions from different greenhouse gases such as carbon dioxide, nitrous oxide, methane and non methane volatile organic carbons (NMVOC), calculated as CO_2-equivalents. Figure 6 shows the carbon footprint contributions made by the different greenhouse gases for the different bleaching sequences in the two scenarios. It is important to note that the biogenic emissions have not been included in the carbon footprint calculations. The greenhouse gas, carbon dioxide, gives the most dominant contribution (81-85%), followed by nitrous oxide (~8%), methane (~6%) and NMVOC (~3%). Most of the nitrous oxide emissions are related to forestry (silviculture).

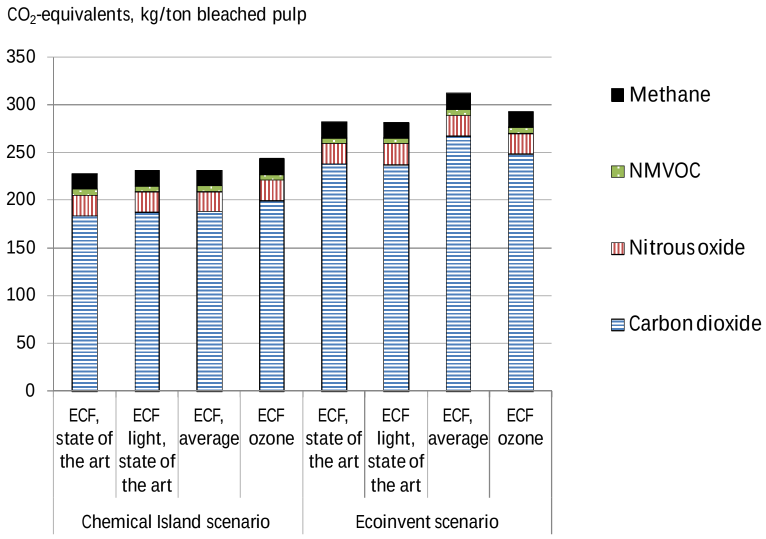


Figure 6: Carbon footprint contributions made by the different greenhouse gases, carbon dioxide, nitrous oxide, methane and NMVOC for the bleached pulp different bleaching sequences in the Chemical Island and the Ecoinvent scenarios.

3.7 Primary energy and other environmental impact categories included in LCA

Primary energy demand is the total energy required by the system, also including extraction and processing of natural resources used to produce both raw materials and energy carriers to produce electricity and heat. It also includes the total energy contained in raw materials, raw fuels and other forms of energy (e.g. hydro power) going into the system. Table 4 below shows the primary energy demand for the alternative bleaching sequences for the two different scenarios. The share of renewable primary energy is also presented; 92% for the Chemical Island scenario and 89% for Ecoinvent. Upstream of the pulp mill, there is a higher share of non-renewable energy, e.g. in:

- production of pulping chemicals and bleaching chemicals cradle-to-gate;
- production of fertilizers and pesticides cradle-to-gate upstream forestry; and
- production of diesel used by forestry machines and for transportation.

There are no big differences in the primary energy demand of the compared bleaching sequences. The results from the Ecoinvent scenario are slightly different compared to those from the Chemical Island scenario. The non-renewable primary energy demand is somewhat higher for the Ecoinvent scenario. The explanation is that in this scenario, there is more non-renewable energy involved in bleaching chemicals production, most importantly in sodium chlorate production.

Although climate change is an important environmental effect, it is only one impact category in LCA. If all the focus is on one impact category, it can lead to sub-optimization. This is why other environmental effects commonly included in LCA, ozone depletion, acidification, eutrophication and photochemical ozone formation, are also included in this study. The purpose of including them is to investigate if there are any significant differences between the alternative bleaching sequences. Table 4 below shows that the differences are small between the bleaching sequences compared. This is the case for all of the environmental impact categories and for both scenarios evaluated.

Table 4. Total primary energy demand, share of renewable primary energy and results for other environmental impact categories included in LCA

	Primary energy (GJ/t)	Share of renewable energy (%)	Ozone depletion potential (kg R11 equiv.)	Acidification potential (kg SO_2-equiv.)	Eutrophication potential (kg PO_4-equiv.)	Photochemical ozone formation (kg ethane-equiv.)
Chemical Island scenario						
ECF, state of the art	45	92	5.8E-06	3.3	1.2	0.46
ECF light, state of the art	45	92	5.8E-06	3.3	1.2	0.46
ECF, average	46	92	5.8E-06	3.4	1.2	0.46
ECF ozone	46	92	6.5E-06	3.4	1.2	0.47
Ecoinvent scenario						
ECF, state of the art	44	89	1.1E-05	3.7	1.2	0.49
ECF light, state of the art	44	89	1.2E-05	3.6	1.2	0.49
ECF, average	45	88	1.3E-05	3.9	1.2	0.51
ECF ozone	45	89	1.2E-05	3.7	1.2	0.50

The environmental effects, human toxicity and eco-toxicity can also be included in LCA. Since LCA is not the ideal method to handle these environmental effects, they have not been included here. When it comes to pulp bleaching there are two types of analytical measures related to emissions to water that are relevant to discuss with regard to toxicity: chemical oxygen demand, COD, and adsorbable organic halogen compounds, AOX. The emissions of COD are included in the quantification of the contributions to the environmental effect eutrophication. The individual substances contributing to the analytical measures COD and AOX would be relevant to include in a risk assessment. This would provide more accurate information rather than using LCA methods to assess the toxicity based on COD and AOX values only. A detailed risk analysis is beyond the scope of the study reported here. What is clear is that the levels of COD after external treatment are comparable for the different bleaching sequences, in the range of 7-9 kg/t of bleached pulp with the ECF ozone sequence on the lower end. The AOX is below 0.2 kg/t of bleached pulp for all sequences.

4. CONCLUSIONS

The conclusions given below are valid for production of elemental chlorine free (ECF) bleached eucalyptus kraft pulp in Brazil.

- 15 - 41% of the total carbon footprint of eucalyptus pulp is made up by bleaching including production of bleaching chemicals cradle-to-gate, transportation of bleaching chemicals to the pulp mill and the bleaching process itself.
    - For the Chemical Island scenario, the contribution from bleaching is 15 - 17%.
    - For the Ecoinvent scenario, the contribution from bleaching is 34 - 41%.

- The alternative bleaching sequences studied result in rather similar carbon footprints of the bleached pulp in the Chemical Island scenario. ECF-state of the art shows the lowest carbon footprint; 227 kg CO_2-equivalents/t, and ECF ozone the highest, 244 kg CO_2-equivalents/t.

- Using data from the public LCA database Ecoinvent, state of the art ECF and ECF light bleaching gave the lowest carbon footprints, 282 kg CO_2 eqv./t, followed by ECF ozone, 293 kg CO_2 eqv./t, and average ECF, 312 kg CO_2 eqv./t.

- There is a large span in carbon footprints of the chemicals used for pulp bleaching. It is crucial to select data that are relevant in terms of geography and technology.
  Both sodium chlorate and sodium hydroxide require large amounts of electricity when produced. The way electricity is produced is strongly influencing the carbon footprint of these two chemicals.

- The carbon footprint of unbleached pulp is roughly made up by:
  - 43-45% from forestry;
  - 44-47% from pulp mill excluding bleaching
  - 6-7% from transport of wood to pulp mill; and
  - 4% from pulping chemicals cradle-to-gate

  assuming that the excess electricity from the mill is exported and replaces electricity produced by the national grid in Brazil.

- A dominance analysis of the relative contribution made by the different greenhouse gases to the total carbon footprint of bleached pulp shows that carbon dioxide gives the most dominant contribution (81-85%), followed by nitrous oxide (~8%), methane (~6%) and non methane volatile organic compounds (~3%).

- For environmental effects other than the carbon footprint, only minor differences between the alternative bleaching sequences have been found.

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