White Paper:

Comparison of Elemental Chlorine Free (ECF) and Totally Chlorine Free (TCF) Bleaching of Softwood Pulps.

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1. Executive Summary

Kraft pulping is an operation of processing wood to solubilize and remove lignin. However, at a certain extent of lignin removal, the kraft pulping process is stopped in favor of more selective bleaching reactions to remove lignin. Bleaching can be performed either with chlorine containing chemicals (chlorine dioxide predominantly) termed ECF or by chemicals with no chlorine termed TCF. Over 96% of the world wide bleached pulp is produced using ECF bleaching due to lower costs, higher pulp quality, lower complexity of technology, and higher reliability.

Yields of bleached pulp at the same pulp strength properties are lower for TCF than for ECF bleaching. The pulp strength for papermaking is expected to be lower for TCF sequences at similar brightness. However no data was found on the impact on pulp quality for use in diapers or other fluff pulp applications. There are examples of residual organic chlorine content in TCF pulp that are higher and lower than for ECF pulp. In addition, levels in both cases are low enough that it is not a relevant factor. The AOX in the effluent is in general higher with ECF sequences, however no correlation was found between low levels of AOX in the paper mill effluents from ECF bleaching sequences and environmental effects. The inorganic chlorate discharge with ECF sequences may be a factor that effects toxicity. The total water effluent discharge from the mill can be significantly lower with TCF than ECF because of the possibility that water from the bleaching process is recycled to replace fresh water usage in the pulping operations.

Life cycle analysis (LCA) is a method to evaluate a product or process impact on the environment throughout its lifetime, considering all life cycle stages (Schenk and White, 2014). LCA of bleached pulp grades indicate that the production of chemicals utilized in pulping and bleaching and the use fossil fuel are the main drivers to most environmental impacts.

When considering environmental aspects of the product of ECF pulp versus TCF pulp, the collection of a consistent, accurate set of mass and energy flows in and out of a pulp mill is paramount. However, there does not exist a reliable set of consistent and current data on existing TCF and ECF pulp mills. This is the challenge of comparing ECF with TCF pulps at this point. One approach is to simulate the pulp and paper mill (ECF and TCF) with a process model (Such as WINGems) that can compute many mass and energy flows based on process knowledge through experiments and secondary literature data. A single LCA study that encompasses both ECF and TCF bleaching processes in a consistent, robust, manner in which the two bleaching systems can be fairly compared and trade-offs identified does not exist. This type of study is critical in understanding environmental differences between products that utilize ECF or TCF bleached pulps.

Cradle to grave LCA of disposable diapers indicate that the sourcing and production of diaper materials contributes the most to environmental impact indicators. This further indicates that the cradle to gate LCA of diaper raw materials is of importance.

2. Kraft Pulping Process

Pulping is the rupturing of bonds within wood either mechanically, thermally, chemically, or by a combination of these treatments. The processes are known as mechanical or chemical pulping. Mechanical pulping uses mechanical energy and small amounts of heat and chemicals and produces weak fibers. Chemical pulping uses chemicals and heat with a small amount of mechanical energy and produces strong fibers. The most common chemical pulping process used in the world for producing bleached pulps is the kraft pulping process. In the kraft pulping process the chemicals used to breakdown the lignin so that the fibers can be separated are sodium hydroxide and sodium sulfide ($NaOH$ and Na_2S). The kraft pulping process is the most common pulping process because it produces the strongest pulp, it can be used to pulp all different species of wood and it has a very efficient chemical recovery process. However the use of the kraft process results in a mill that creates an odor and the kraft pulp is dark compared to the sulfite pulping process and is more difficult to bleach.

The kraft process removes the lignin from the wood but a significant amount of the hemicellulose and cellulose are also removed. As a result, the typical yield of the kraft process is about 50%. The portion that does not become wood is however burnt in a boiler to generate energy to operate the mill. In producing bleached kraft pulp, the removal of the lignin is somewhat selective early in the cook when there is a lot of lignin in the wood but then becomes less selective and causes yield losses later as shown in **Figure 2.1** (Seuss, 2010, pg 48). Kappa number is a measure of the amount of lignin left in the pulp, and typically softwoods are pulped to 30 kappa (4.5% lignin) and hardwoods are pulped to 16 kappa (2.4% lignin) before the pulping process becomes less selective. It should be noted that hardwoods are always easier to pulp than softwood because the lignin in hardwoods are significantly easier to degrade. As a result, softwoods require more chemicals to pulp and bleach resulting in higher cost and bleaching effluent loads.

To decrease the environmental impact of bleaching it is important to remove as much lignin in the pulping process as possible without hurting pulp end use properties. Some mills use modified kraft pulping processes to decrease the kappa number to less than 30 for softwoods and 16 for hardwoods. The lowering in the kappa number results in lower chemical usage in the bleach plant and is especially important for TCF bleaching sequences.

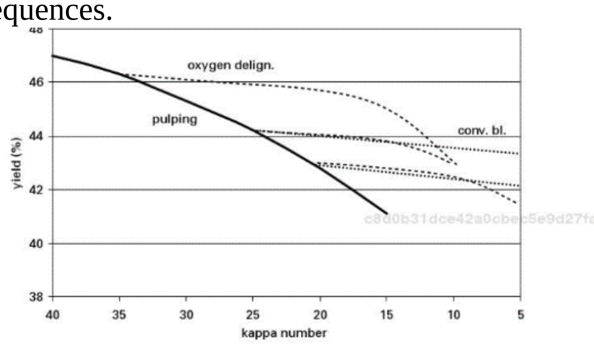


Figure 2.1. Overall pulp yield as a function of lignin removal for kraft pulping, oxygen delignification (dashes), and bleaching (dotted).

3. Bleaching

Bleaching is the process that is used to destroy and remove color causing components in pulp, thereby increasing the brightness and whiteness and decreasing the color. Bleaching of mechanical pulps leave the lignin in the pulp (example: newsprint) while bleaching of chemical pulps uses chemicals which dissolve and remove the lignin (fluff pulp, white printing and writing grades). Mechanical pulps are bleached by only destroying the chromophoric groups in the lignin, with very little lignin removal. Usually only chlorine free chemicals are used for bleaching mechanical pulps. Some mechanical pulps have been used in diapers but their performance is lower than that of bleached chemical pulps, since lignin is hydrophobic and will affect water absorption. For chemical pulps, bleaching removes the lignin left from pulping and destroys any chromophoric groups left in the pulp. Chemical pulps have essentially no lignin left after bleaching. Bleaching is usually much more selective than pulping and the yield losses are lower than for both conventional and extended pulping as shown in **Figure 2.1**. Thus, bleaching operations, are used as a selective method for further delignification.

Bleaching is commonly done in multiple stages with different chemicals in consecutive stages with conditions and reactants in each stage (DOE, 2005) to minimize cost and pulp degradation. A bleaching stage consists of mixers, a reaction vessel and a washer. The washer uses water to remove the degraded wood components and the bleaching chemicals from the pulp and may need to be discharged. Most of the chemicals used are oxidants that break down the lignin or react with the chromophoric groups. Typical chemicals used in an elemental chlorine free (ECF) sequences are shown in **Table 3.1**. In most sequences acidic stages are followed by an alkaline extraction, to dissolve the reacted lignin. Examples of the most common bleaching ECF sequences include D(EOP)DED, D((EOP)DP. As can be seen in both of these examples, a chlorine dioxide stage (D) is sometimes followed by an alkaline extraction stage (E). **Table 3.2** defines the bleaching stages denoted by the abbreviations (Suess, 2010).

Table 3.1. Common bleaching chemicals.

Chemicals	**Function**	**Advantages**	**Disadvantages**
Chlorine Dioxide	Oxidize lignin Brighten pulp	High brightness Low pulp degradation Very selective to lignin	Make on site Can be expensive
Hydrogen peroxide	Oxidize lignin Brighten pulp	Easy to use	Can be expensive
Sodium hydroxide	Solubilize lignin	Cheap	Darkens pulp
Oxygen	Oxidize land solubilize lignin	Effective Cheap	High capital cost Loss of pulp strength

Table 3.2. Bleaching stage designations.

Table 4.1 Bleaching stage designation, usual conditions and effect achieved

O	oxygen stage for oxidation of lignin, using molecular oxygen under alkaline conditions at 90 °C to 100 °C.
A	acid stage to remove transition metals (at 40 °C to 60 °C) or (at >90 °C) hexenuronic acid by hydrolysis, the acid typically used is sulfuric acid.
Q	acidic stage (pH 5 to pH 6.5) with chelating agents (such as EDTA or DTPA) for removal of transition metals.
D	chlorine dioxide stage using a solution of ClO_2 at pH <5 in water for lignin oxidation.
E	extraction stage using caustic soda for solubilization of oxidized lignin (pH 9.5 to 11).
Eo	extraction with addition of oxygen gas for improved lignin removal by oxidation.
Eop	extraction reinforced with oxygen and hydrogen peroxide for improved lignin removal by oxidation and brightening.
P	alkaline bleaching stage with hydrogen peroxide, (pH >10 to 11, 60 °C to 90 °C).
OP	pressurized peroxide stage with addition of oxygen, potentially operated above 100 °C with up to 0.3 MPa pressure.
Z	delignification stage with gaseous ozone.
Paa	weakly acidic stage (pH ~5) with peracetic acid for lignin oxidation and activation of a subsequent P stage.
X	enzyme treatment stage with xylanase or other hemicellulases to improve lignin accessibility by removal of precipitated carbohydrates.
Y	reductive treatment with dithionite.
n	neutralization.

Note: Bleaching sequences are described by combining these letters, for example: ODED. In this combination the washing procedure between the stages is not explicitly mentioned. It is assumed to take place as this is the common procedure. A combination without intermediate washing can be indicated by the use of brackets: (ZD). The way of combining the letters is not standardized. Sometimes in a combination of letters the capital letter is used to describe the main purpose of the stage, the combination "Eo" stands for an extraction stage with a support of the extraction by oxygen addition. Sometimes the description EO is used for the same purpose. A glossary of Bleaching Terms is available at [1].

In kraft pulp mills degraded lignin and cooking chemicals are sent to a recovery area that regenerates the pulping chemicals and produce energy. However, if a bleaching stage uses any chlorine containing chemical, the filtrate from the washer cannot be recycled to the recovery system and must be discharged from the mill. Chlorine bleaching chemicals cannot enter the chemical recovery system due to the corrosive nature of chlorine containing compounds. Most of the water used in pulping is recovered and very little effluent is discharged, however all the water used in a conventional ECF bleach process needs to be discharged. Typical water usage from different parts of the mill are shown in **Table 3.3** (Jameel, 2002). The bleach plant is the largest user of fresh water in a conventional pulp mill.

Table 3.3. Water usage in ECF bleaching mill for older and newer technology.

Table 1: Water usage in various process areas of a bleached kraft mill (m^3/admt)

Area	Older Mill	Newer Mill
Digesting	1.1	1.0
Washing & Screening	4.2	1.8
Bleach Plant		
Acid Effluents	25.0	21.0
Alkaline Effluents	30.0	10.0
Chemical Preparation	0.5	0.8
Total Fiberline	60.8	34.6
Pulp Machine		
Rejects	1.3	1.3
General	5.2	4.9
Total Pulp Machine	6.5	6.2
Evaporators	0.7	0.6
Recovery	2.1	0.6
Hog/Power Boiler	4.9	0.9
Recausticizing	2.6	1.3
Total Recovery/Power	10.3	3.4
Grand Total, m^3/admt	77.6	44.2

In an effort to decrease the environmental impact of bleaching, oxygen delignification has been used to extend lignin removal selectively. Oxygen delignification is more selective than pulping; however, it also suffers from lack of selectivity at low lignin contents compared to bleaching, **Figure 2.1**. Any water used in oxygen delignification can be recovered and does not need to be discharged. Typical ECF softwood bleaching lines with oxygen include OD(EOP)D(EP)D, (OO)D(EOP)DnD or OD(EOP)DP (Suess, 2010).

Oxygen delignification and extended delignification can be used in combination to decrease the kappa number entering the bleach plant even further. The use of TCF sequences usually require both oxygen delignification and extended delignification, **Figure 3.1** (Crennel, 1995). In the figure the effluents that can be sent to the recovery area and the discharged effluents are indicated with left and downward arrows, respectively.

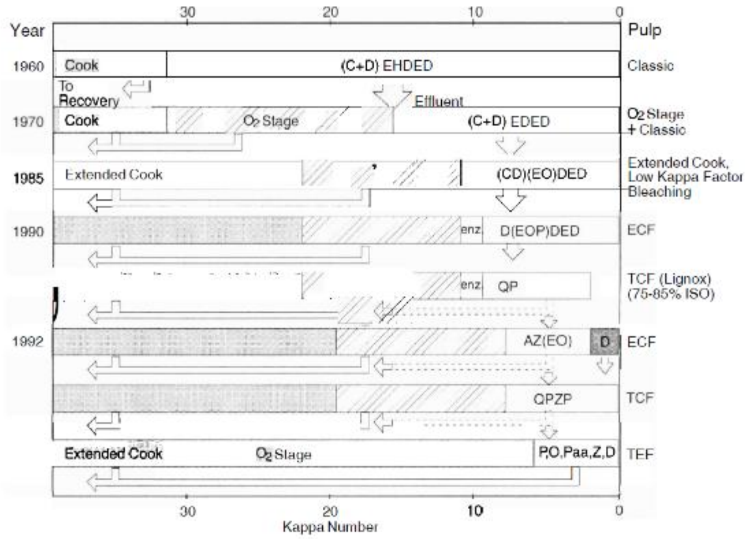


*Fig. **6**. Schematic illustration of the development of delignification and bleaching of* ***softwood*** *kraft pulp. Paa = Peracetic acid, A = acid, and Q = chelating agent.*

Figure 3.1. Evolution of pulping processes with the degree of delignification and indication of how effluents are either recycled (left arrows) or discharged (down arrows).

There is always a decision to be made pertaining how much delignification needs to occur before bleaching when considering the following three phenomena:

- Pulp yield on wood
- Chemical demand in bleaching
- Impact on effluent treatment

It is clear that extended cooking and oxygen delignification reduce chemical demand in bleaching and reduce bleaching effluents, at some expense of pulp yield.

4. ECF-TCF Bleaching: Chemicals Used

Total chlorine free (TCF) bleaching uses no chlorine, whether in elemental or combined form, whereas elemental chlorine free (ECF) bleaching uses chlorine in combined form (Chlorine dioxide, D, in **Table 3.1 and 3.2**) but not in elemental chlorine form, Cl_2.

ECF pulps can be bleached with or without oxygen delignification. Typical chemical charges for non-oxygen bleached softwood are: 40 kg/t chlorine dioxide, 30 kg/t caustic soda, 5 kg/t oxygen and 5kg/t hydrogen peroxide. For oxygen bleached pulps: 20 kg/t chlorine dioxide, 18 kg/t caustic soda, 5 kg/t oxygen and 5kg/t hydrogen peroxide.

TCF bleaching uses two or more oxygen delignification stages, but these suffer from lower yields than bleaching. Peroxide (P) is also used as a bleaching stage or an enhancement to an oxygen stage (Op) but requires a Q stage which involves acidifying to less than 3 pH or to 5 pH along with chelating agents in order to remove metals that interfere with peroxide treatment. In general TCF requires higher charges of oxidizing chemicals, such as 7kg/t ozone, 35 kg/t peroxide, 40kg/t caustic soda, 10kg/t EDTA chelant (Suess, 2010, pg 170).

In 2005 it was reported that 96% of the total US bleached production was ECF (DOE, 2005, page 58). Of the 222 softwood kraft bleach lines (suitable for producing hygiene softwood kraft fibers) in the world in 2015, only four have reported that they are using TCF bleaching (one in China and three in Sweden), see **Table 4.1**. The amount of TCF softwood bleached pulp produced annually, 1.4 million tons, is only 3.5% of the total of 38 million tons of softwood bleached pulp.

Table 4.1. The Monsteras and Varo mill are owned by Sodra Cell. The Ostrand mill is owned by SCA. The Yongzhou mill is owned by Xiangjiang Paper Mill Co., Ltd. (needs to be verified).

Site Name	Site Shipping City	Fiber Type	Fiber Origin	Bleach Sequence	Sum of TPY Queried Pulp by Line, ADMT	Days Operated	TPY of Species
Yongzhou City	Yongzhou City	Softwood	Southern	O2-O2-P	61,707	190	33,498
Monsteras	Monsteras	Softwood	Northern	O2-O2-Q-Op-PAA/Q-PO	626,430	266	476,087
Varo	Varobacka	Softwood	Northern	O2-O2-Q-Op-PAA/Q-PO	420,144	350	420,144
Ostrand	Timra	Softwood	Northern	O2-Q-Op-Zq-PO	429,616	355	435,753
							1,365,482

Some common chemicals used in TCF bleaching and their advantages and disadvantages are listed in **Table 4.2.**

Table 4.2. Chemicals used in TCF Bleaching

Chemicals	**Function**	**Advantages**	**Disadvantages**
Ozone	Oxidize lignin	Effective	Cost Poor particle bleaching Loss of pulp strength
Hydrogen peroxide	Oxidize lignin Brighten pulp	Easy to use	Can be expensive
Sodium hydroxide	Solubilize lignin	Cheap	Darkens pulp
Oxygen	Oxidize and solubilize lignin	Effective Cheap	High capital cost Loss of pulp strength
Peracids	Oxidize lignin Brighten pulp	Effective	Cost Pulp strength Metallurgy
Enzymes	Catalyze xylan removal	Easy to use Low capital cost	Limited effectiveness Cost
Chelants	Remove metal ions	Improves peroxide bleaching	Cost

5. ECF-TCF Bleaching: Impact on Yield

ECF pulps have higher yield than TCF pulps in general, thus being a more efficient process with regards to wood utilization. The overwhelming consensus from paper manufacturers is that ECF provides pulps relative to TCF that at the same strength properties have about a 4% higher yield (CPI, 2013). In addition, ECF pulps with 4% higher yield than TCF pulps at the same strength properties are brighter, less expensive *and have negligible differences in environmental impacts* (CPI, 2013).

Popp states that early yields from TCF pulps were lower requiring more wood and that the use of TCF to obtain high brightness pulps resulted in lower fiber strength and that bleaching costs were 40-50% higher than ECF bleaching (Popp et al, 2007, page 7). TCF bleaching does not delignify shives and bark in the pulp as well as does ECF bleaching, necessitating a more efficient mechanical screening with accompanying yield losses (Suess, 2010, page 171). Vuorenverta (Suess, 2010, page 171) found a 42.5% yield for ECF pulp and 41.3% yield for TCF pulp.

Yield losses from using TCF bleaching have been reported to be 10kg/t higher than ECF (Suess, 2010, page 183). For a 2000 tons per day mill, TCF bleaching will dissolve an additional 40 tons per day of fiber relative to ECF bleaching, not only significant with respect to yield losses, but also representing a significant increase in effluent loading. **Table 5.1** (Suess, 2010, page 184) are experimental results that show TCF having a lower yield and higher COD than ECF.

Table 5.1. TCF and ECF bleaching process results.

Table 4.10.5 Comparison of TCF and ECF bleaching of Kraft pulp. Sequence in TCF with OP and (PO) stages at 90 °C and 100 °C, OP with 10 kg/t H_2O_2, (PO) with 30 kg/t H_2O_2. Ozone amount 5 kg/t, peracetic acid amount 10 kg/t [7].

	Sequence	Oxygen del. kappa	Brightness (%ISO)	Yield (kg/t)	COD (kg/t)	Ratio COD/loss
spruce/pine	OQ(OP)Z(PO)	15	87.3	93.9	60.5	1.01
spruce/pine	OQ(OP)Paa(PO)	15	85.2	94.1	58.6*	1.01
spruce/pine	ODEopDP	15	>88	96.0	40.2	0.94
eucalyptus	OQ(OP)P	9	90.3	94.7	52.8	0.99
eucalyptus	DEopDP	8.8	90.5	98.1	18.6	0.98

* analyzed value decreased by 10.7 kg/t for the COD equivalent of 10 kg/t acetic acid

6. ECF-TCF Bleaching: Impact on Kraft Process

As a TCF bleaching process is implemented it effects the overall kraft recovery cycle since more of the bleaching effluents are recycled as shown in **Figure 6.1**. There will be additional organic and inorganic loads on the recovery boiler because a significant amount of the chemicals and lignin from the bleach plant are recovered. This results in slightly higher energy recovery but more of the chemicals also have to be regenerated.

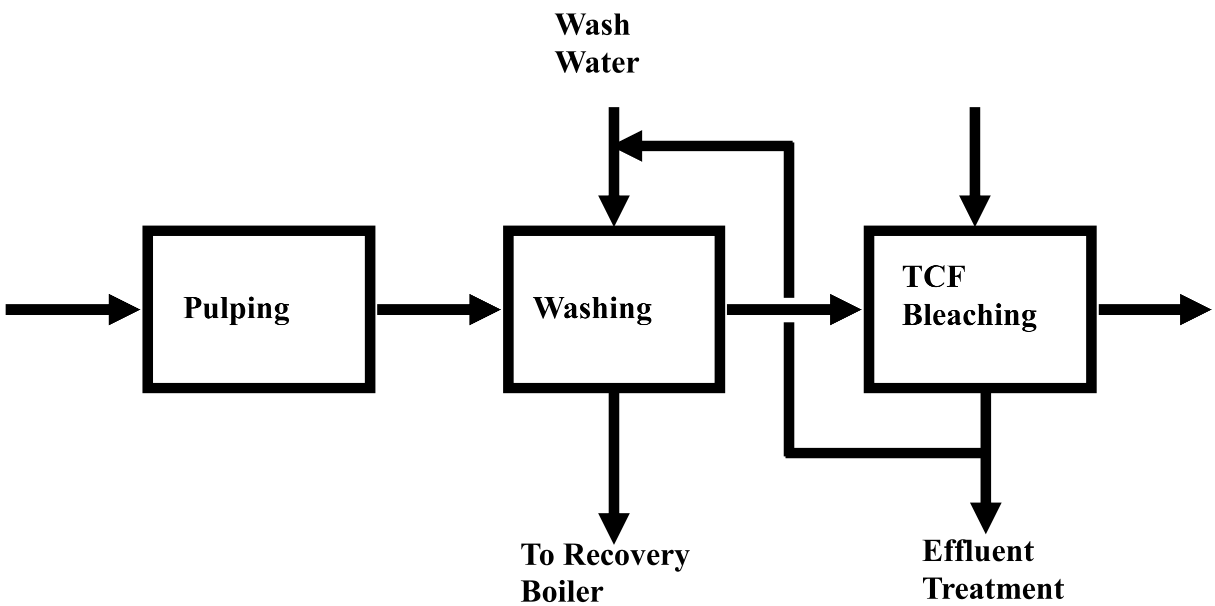


Figure 6.1. Flowsheet showing that effluent from TCF bleaching may be sent to washing and the recovery boiler; for ECF bleaching this is not the case.

An important impact of the increased recycle of the water using TCF processes is the buildup of non-process elements (NPE) in the recovery cycle which can lead to increased scaling, dead-load, corrosion and decomposition of bleaching chemicals. A mill will have to discharge more of the precipitator dust generated in the exhaust stack of the recovery boiler to flush the system, necessitating more purchase of chemical make ups. Other technologies are being developed to decrease the impact of the NPEs such as leaching of the wood chips and the use of membranes, but these are exotic and are not practiced currently. Increased closure of the bleach plant also makes the process more susceptible to upsets and increases the demands on the overall process control systems.

7. ECF-TCF Bleaching: Impact on Pulp Physical Properties

Yang shows in lab data that at the same brightness pulp that ECF relative to TCF pulps have less fiber degradation (higher viscosity of cellulose) and higher tensile-tear strength relationships (Yang, 2003). Sundquist states that fiber length is decreased due to TCF bleaching (Suess, 2010, page 170). To overcome a strength loss from decreased fiber length, more beating (higher energy input) was required to develop strength. Popp concludes that the use of TCF to obtain high brightness pulps results in lower fiber strength (Popp et al, 2007, page 7).

The World Business Council on Sustainable Development (WBCSD) and the World Resources Institute (WRI) website "Most of the global paper industry has phased out the use of Elemental Chlorine as a bleaching agent; however, some facilities still use it. The prevailing bleaching systems are Elemental Chlorine Free (ECF) and Enhanced Elemental Chlorine Free (EECF). Total Chlorine Free (TCF) bleaching may be an option for certain products although it tends to use more fiber and produce a lower quality product." (World Resources Institute, 2015)

Weyerhaeuser company concurs with this viewpoint: "ECF bleaching technology, which substitutes chlorine dioxide for elemental chlorine, greatly reduces, to the extent of being nondetectable, the incidental formation of unwanted chlorinated organic compounds… several studies by industry experts have concluded that ECF bleaching provides higher yield and produces stronger fibers compared to TCF bleaching for pulps at similar brightness. To compensate for the yield and strength loss, products made from TCF pulp require additional fiber resources compared with products made from ECF pulp. TCF pulp also generally costs more per ton to produce than ECF pulp. Therefore, it is questionable that chemical pulp produced with TCF bleaching provides any significant environmental advantage relative to ECF bleached pulp, which is why Weyerhaeuser considers ECF bleaching the most innovative and advanced pulp bleaching technology available and has implemented it at all of its pulp mills." (Weyerhaeuser, 2015)
It is generally concluded that ECF is greatly preferred technology than TCF for its lower cost, **Figure 7.1 (**Rennel, 1995), higher pulp yield, (Suess, 2010, page 171) and higher resulting pulp strength (DOE, 2005).

No data has available that shows the performance of ECF vs TCF pulps for use in absorbent products.

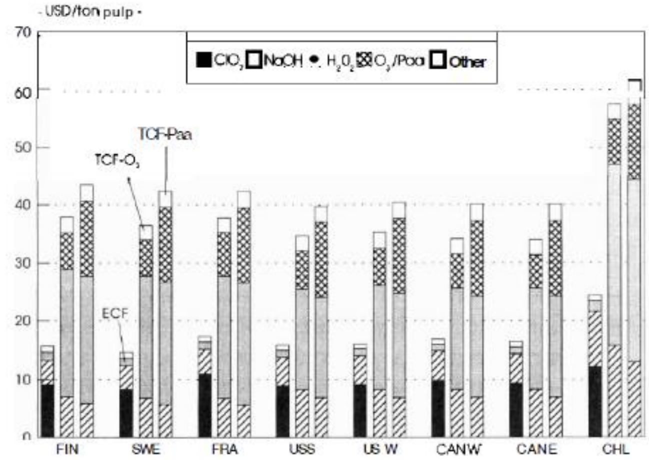


Fig. 7. Costs of bleaching chemicals after oxygen delignification for new ECF and TCF softwood kraft pulp mills in different regions (cost level 1994:3rd quarter). (CHL = Chile.)

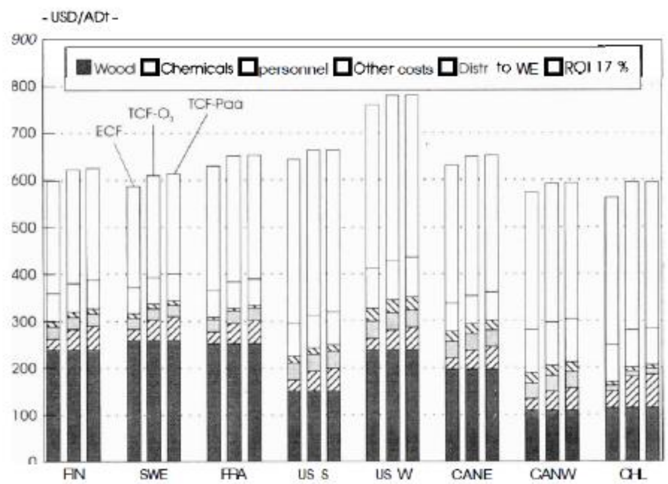


Fig. 9. Sales price requirements for new hypothetical BSKP mills producing ECF and TCF pulp, respectively, for deliveries to the Western European market, (capacity 500 000 t/a, cost level 1994:3rd quarter).

Figure 7.1. Cost of bleaching chemicals for ECF and TCF (top) and the sales price required for sustainable sales of ECF and TCF pulps in Western Europe (bottom).

8. ECF-TCF Bleaching: Impact on Organic Halide in Pulp

Another topic to discuss is the organic halide (OX) that is residual in the pulp after bleaching with chlorine, with ECF and with TCF bleaching (Suess, 2010, pages 103-107). With chlorine bleaching OX has been reported in the range of 400 to 1200 g/ton pulp (**Table 8.1**) and for ECF about 100-250 g/ton pulp (**Figure** 8.1).

Table 8.1. Residual halogenated organic matter in pulp for chlorine bleaching and ECF bleaching sequences.

Table 4.4.3 Impact of bleaching sequence and lignin removal on remaining halogenated organic matter in semi bleached pulp. Softwood Kraft pulp, kappa 27.5, substitution level in Cd at 20%. Final P stage with 4 kg/t H_2O_2 [45].

Sequence	Active Cl in H or D (kg/t)	Final kappa	Brightness (%ISO)	OX (g/t)
CEH	30	1.7	73.8	1.210
CdEoD	15	1.3	77.3	640
CdEoDP	15	0.9	82.8	420

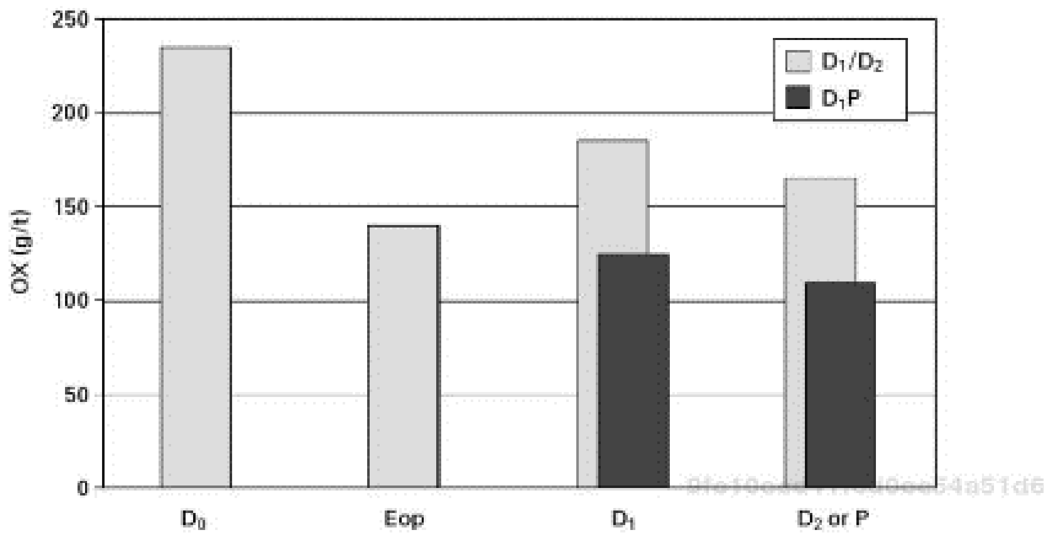


Fig. 4.4.34 Impact of ECF bleaching on halogenated residual in pulp. Eucalyptus Kraft pulp, oxygen delignified to kappa 11.8. Application of 12 kg/t active chlorine in D_1D_2 and 3 kg/t in D_1P (+2.5 kg/t H_2O_2), final brightness >90% ISO [46].

Figure 8.1. Residual halogenated organic matter in pulp for ECF bleaching sequences.

TCF pulps have OX in them due to the natural chloride ion in water that is transformed due to TCF bleaching conditions into OX in the product, **Figure 8.2**, (Suess, 2010 page 106). An artificial definition of TCF pulps are that they have less than 30 g OX/ton pulp (Suess, 2010 page 106). However, examples of ECF pulps with 18 g/ton pulp and of TCF pulps with 100-200 g/ton have been presented.

It has been concluded by Seuss (Suess, 2010 page 107) that these low levels of OX are not relevant. Furthermore, he states that there is no indication that most compounds that contribute to OX are toxic. His conclusion is that levels of OX are not pertinent to the determination of ECF and TCF bleaching processes being better or worse environmentally.

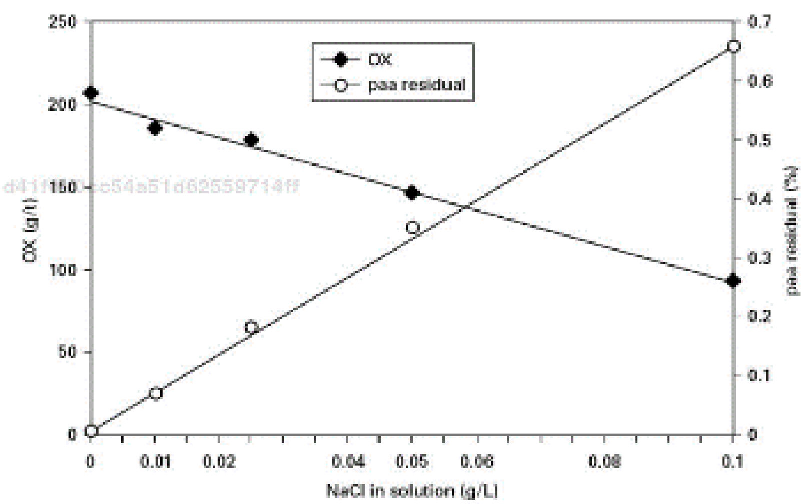


Fig. 4.4.36 Effect of trace amounts of sodium chloride in a final peracetic acid stage on OX residual and consumption of peracetic acid. Softwood Kraft pulp, sequence O(AQ)(OP)Paa, constant 10 kg/t distilled peracetic acid, 75 °C, 1 h, 10% consistency [48].

Figure 8.1. Residual halogenated organic matter in pulp for TCF bleaching sequences. Note that the OX in these pulps can be higher than in ECF pulps.

Organic halides are common in nature, originating mainly from wood fires, volcanic activity, and marine algae. They are also produced in humans, animals and plants that are necessary for life. Seuss emphasizes that 5 million tons of chloromethane are produced in nature per year and only 30,000 tons are produced from all industry, about 0.5% of the total (Seuss, 2010, page 102). Of the 0.5% the paper industry is only a fraction of all industrial production. The fact that organic halides are naturally formed in nature, that industry and the pulp and paper industry contribute a very small portion of the total, that there is no evidence that they are toxic, and that ECF and TCF have been shown to have the overlapping levels in paper, it is concluded that there is no practical significant difference between OX in ECF and TCF products. In fact, chlorine and other halogens are found in nature bound to organics as a necessary used component in the metabolism of microorganisms, algae, plants and higher species

9. ECF-TCF Bleaching: Environmental Discussion Water

The water usage in a TCF mill is expected to be significantly lower than conventional technology, Table 9.1 (**Jameel, 2002**). The water usages for the TCF mill with partial closure is shown below. There are very significant reductions in water usage in the bleach plant. Attempts have been made to close ECF mill by closing up the water circuits. Trials were run in Thunder Bay (Reeve, 1982) in the 70's but they were discontinued due to corrosion issues and high operating costs. At present there is very minimum recovery of bleach plant effluent.

Table. 9.1. Water usage for ECF and TCF technologies, m3 of water per air dry ton pulp.

Area	**Conventional Modern ECF Bleaching**	**TCF**
Digesting	1.0	1.0
Washing & Screening	1.8	1.0
Bleach Plant		
Acid Effluents	21.0	0
Alkaline Effluents	10.0	5.0
Chemical Preparation	0.8	0.8
Total Fiberline	34.6	7.8
Pulp Machine		
Rejects	1.3	1.3
General	4.9	4.9
Total Pulp Machine	6.2	6.2
Evaporators	0.6	0.6
Recovery	0.6	0.6
Hog/Power Boiler	0.9	0.9
Recausticizing	1.3	1.6
Total Recovery/Power	3.4	3.7
Grand Total, m^3/admt	44.2	17.7

The organic matter in the bleach plant effluent is a very complex mixture of chemicals with a range of chemical structures and molecular weight. More than 300 low molecular weight organic compounds have been identified in the bleach plant effluents. Since there is a wide range of chlorinated compounds present, they are measured as Adsorbable Organic Halide (AOX). From an environmental standpoint, the reduction of adsorbable organic halide (AOX) is a significant reason to use ECF or TCF relative to elemental chlorine bleaching. In general, about 10% of the Cl_2 ends up reacted to the organics whereas only 2% of ClO_2 as Cl does (Suess, 2010 page 99). The reduction in AOX in kg/air dry tonne when using ECF is shown in **Figure 9.1** (Rennel, 1995). Note that an oxygen delignification stage reduces AOX significantly as does the removal of ClO_2 in the first stage of bleaching where the lignin content of the pulp is relatively high. This is not commonly practiced in most ECF bleaching sequences.

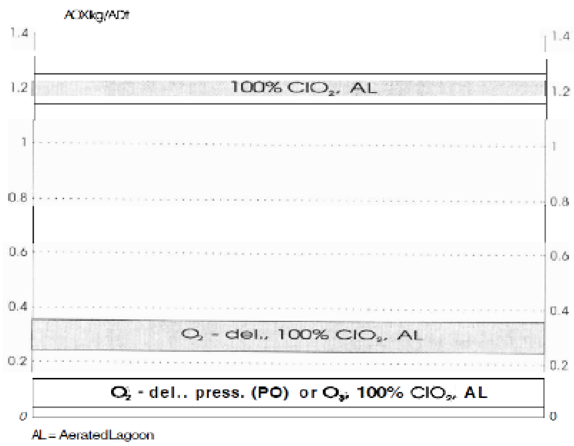


Fig. 2. Impact of different AOX levels on technology applied in existing pulp mills in the USA.

Figure 9.1. AOX in the bleach effluents after an aerated lagoon treatment.

A similar result from lab studies is shown by Suess (Suess, 2010 page 98) for the C(D)EopDEpD sequence showing that the substitution of ClO2 for Cl2 reduces AOX by about 66%, **Figure 9.2.** TCF pulps are considered to have zero AOX in the effluent.

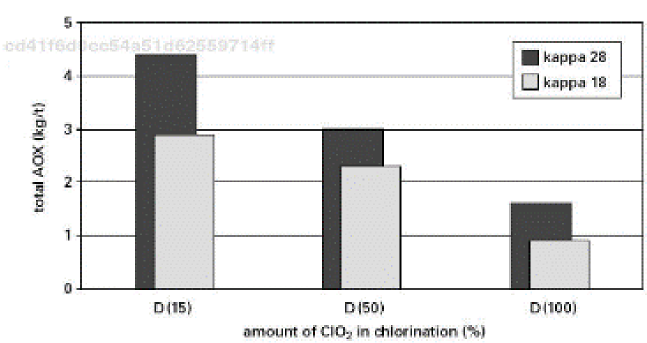


Fig. 4.4.29 Impact of increasing chlorine dioxide substitution in a C(D)EopDEpD sequence on the total amount of AOX [34]. Constant kappa factor 0.17. All pulps bleached to full brightness.

Figure 9.2. AOX in effluents from lab bleaching using chlorine and ECF bleaching stages. Lower kappa/lignin and higher substitution of ClO2 for Cl2 reduces AOX.

It should be noted that different mills have very different AOX releases, **Figure 9.3** (Rennel, 1995).

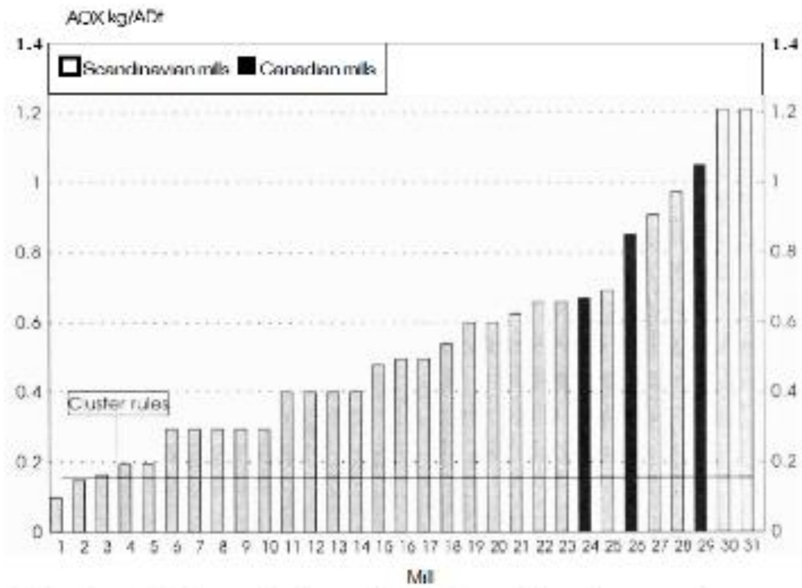


Fig. 3. AOX emissions from Scandinavian and some Canadian bleached kraft pulp mills in 1994.

Figure 9.3 AOX emissions from several mills.

It has also been concluded that AOX measurements have no direct correlation with toxicity (Suess, 2010 page 102).
While TCF provides lower AOX than ECF, TCF does not necessarily have lower dissolved organics or inorganic chemicals (that are nutrient compounds) in the effluents. As stated by Rennel in 1995, "It cannot be argued that TCF pulps or their end products are more environmentally friendly than those from the ECF process."

Cates et al (1995) showed in careful lab experiments that TCF effluents had higher chemical oxygen demand (COD) and total organic carbon (TOC), both indicative of dissolved organic materials, than did ECF (**Figure 9.4**). This was due to the non-specificity of the ozone and hydrogen peroxide stages in the TCF bleaching. It should be pointed out that in most cases the TCF effluents are recycled back into the recovery process and this increased amount of COD has little environmental impact.

TOC and COD are two ways of measuring effluent contributions to the receiving body of water that will promote biological activity and corresponding removal of oxygen from the water. TOC is a material and contributes to COD. BOD (biological oxygen demand) and COD are actually not materials, but are characteristics of effluent that reflect how much oxygen might be taken up by introducing the effluent into water. However, they are considered to contribute to eutrophication in the same way a mass flow would, **Table 9.2.** It should be noted that a tested sample of water effluent does not have separate species that contribute to COD or BOD only, organic material can contribute to both the COD and BOD of a sample.

Depending on the mill water management, it is expected that the concentration of COD, BOD and TOC to be lower for TCF than ECF pulping because the TCF mills could be recycling bleach plant effluent to the recovery system. However, some TCF mills have had issue with high degrees of recycling due to scaling and corrosion. At this point we don't have any data on the water recycling practices of current practicing TCF mills. This could be addressed by collecting data from existing TCF mills and process simulations.

In the same study, the color of the effluent was found to be very low for both TCF and ECF; however a color was found for the ECF bleached softwood effluent (280 CU) greater than the color of TCF bleached softwood effluent (175 CU).

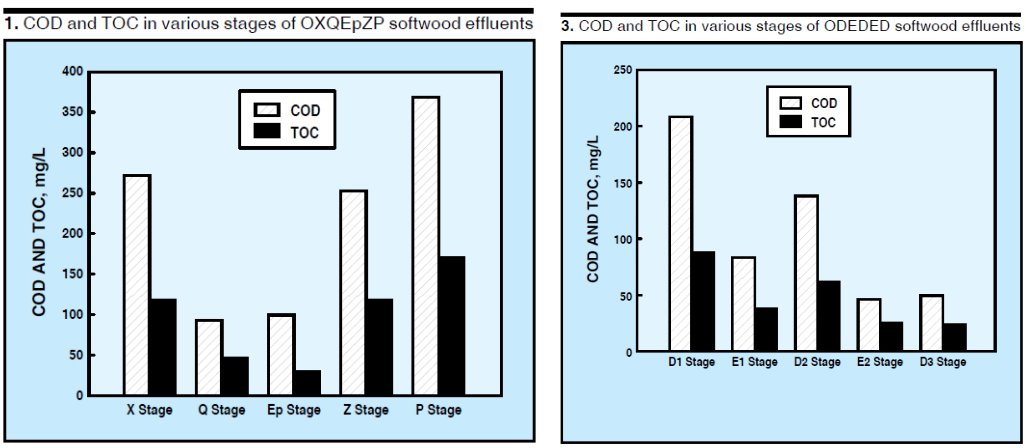


Figure 9.4. COD and TOC for ECF and TCF lab bleaching experiments.

Table 9.2 Substances and their characterization factors contributing to eutrophication in the EPA TRACI Model.

Substance Name	Eutrophication Air (kg N eq / kg substance)	Eutrophication Water (kg N eq / kg substance)
PHOSPHORUS	1.12E+00	7.29E+00
PHOSPHORUS PENTOXIDE	4.90E-01	3.19E+00
PHOSPHATE	3.66E-01	2.38E+00
PHOSPHORIC ACID	3.55E-01	2.31E+00
NITROGEN	1.50E-01	9.86E-01
AMMONIUM	1.19E-01	7.79E-01
AMMONIA	1.19E-01	7.79E-01
NITRIC OXIDE	6.86E-02	4.51E-01
NITROGEN DIOXIDE	4.43E-02	2.91E-01
NITROGEN OXIDES	4.43E-02	2.91E-01
NITRATE	3.60E-02	2.37E-01
NITRIC ACID	3.45E-02	2.27E-01
BIOLOGICAL OXYGEN DEMAND	0.00E+00	5.00E-02
CHEMICAL OXYGEN DEMAND	0.00E+00	5.00E-02

Toxicity was shown to be higher for untreated effluents for ECF versus TCF and the ClO2 in the ECF bleaching was responsible for this (Cates et al, 1995). However, after fungal treatment with T. versicolor, no toxicity was observed for both TCF and ECF pulp effluents, **Table 9.3.** Effluents from paper mills undergo secondary treatment before being discharged. Secondary treatment was designed to remove biological oxygen demand (BOD) of the discharge, but they have also been effective in reducing toxicity and AOX. More than 90% of the BOD can be decreased by an aerated lagoon. Reductions of AOX have also been reported but there is significant scatter in the data. 30 to 60% decrease in AOX have been reported (Hagiland et al 1991, Gergov et al 1988). Reduction of AOX from ECF sequences may be higher than for sequences containing chlorine due to the higher percentage of low molecular compounds in the efflent (O'Conner et al 1993). Bleach plant effluents from softwood fluff produced by ECF and TCF showed no or low toxicity in test using zebra fish (Brunsvik et al 1991, Flink et al 1993). In another study (Chirat et al 1993), TCF effluents exhibited lower toxicity than a ECF effluent. The overall conclusions are that with conventional effluent treatments at the mill, primary and secondary biological treatments, that no toxicity exists in either ECF or TCF effluent discharges.

Some of the inorganic compounds in the effluents from bleaching can also contribute to toxicity. The chlorate produced during bleaching with chlorine dioxide is known to be toxic.

Table 9.3 Toxicity of ECF and TCF effluents before and after fungal treatment. EC50 values of >1.00 indicate no toxicity.

IV. Toxicity of effluents before and after incubation with *T. versicolor* (based on Microtox 15-min EC_{50} values)

TCF softwood	EC_{50}*
Day 0	0.56
Day 6	>1.00
ECF softwood	
Day 0	0.24
Day 6	>1.00
TCF hardwood	
Day 0	>1.00
Day 6	>1.00
ECF hardwood	
Day 0	0.47
Day 6	>1.00

*Lower figures indicate higher toxicities.

Specific compounds such as 2,3,7,8 tetra chlorinated dibenzodioxin and 2,3,7,8 tetra chlorinated dibenzofuran **Figure 9.5** are not generated by ECF mills (Suess, 2010 page 102). This was verified by a detailed study of pulp mills in Maine (Pryke and Barden, 2006). Forest fires and waste incineration in which organics and chloride are present naturally are much larger sources of these compounds than pulp bleaching (Suess, 2010 page 102). Further, modern pulping and bleaching technology combined with effluent treatment can lower AOX to extremely low levels, such as a recent report of 0.09 kg/ton for bleached hardwood mill (Landim et al, 2005; Suess, 2010 page 102; Rennel, 1995).

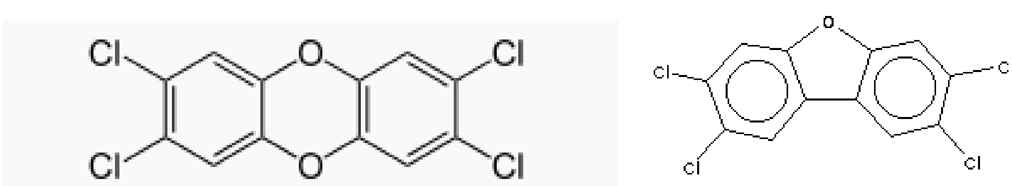


Figure 9.5. 2,3,7,8 tetra chlorinated dibenzodioxin (left) and 2,3,7,8 tetra chlorinated dibenzofuran (right)

In order to investigate if ECF and TCF bleaching methods produce safe pulp for use in sanitary product like diapers, studies were conducted to validate that the pulp manufacturing plants that replaced elemental chlorine gas bleaching with ECF or TCF bleaching. The results show no signs of dioxin being present in pulp, emissions, or in fish downstream from the plant. (P&G, 2015; Hamm and Göttsching, 2002).

The cluster rules in 1997 tried to set up TCF as best available technology (BAT) but industry opposition caused the EPA to weaken its proposed limits on AOX allowing ECF to be the best available technology BAT and setting an AOX limit of 0.62 kg/ton pulp (Popp et al, 2007). Some key regulations pertaining to AOX are shown in **Table 9.4.** Other regulations have motivated the switch to ECF pulps (Popp et al, 2007 page 34).

The laboratory results showing no toxicity after aerated lagoon treatments for both ECF and TCF pulps, the pulp mill study showing no detectable dioxin type compounds for ECF pulps, the fact that production of all natural organic halides are at least 200 fold higher than that from industry, that there is no correlation between AOX and toxicity, the wide spectrum of AOX generated in ECF mills, it is concluded that there does not exist a practical significant difference in AOX between ECF and TCF pulps. Table 9.4. Regulations on AOX.

Table 4 – Summary of Key Regulations

Sweden

1991: Environmental legislation establishes strict guidelines for AOX (**0.1-0.2 kg/t**). Enforcement is through plant-by-plant permitting.

Finland

1987: Issues first guidelines for AOX (**1.4 kg/ADT**), to be met by 2004. Enforcement is through plant-by-plant permitting.

1993: Accepts Nordic Working Group performance standards for AOX (**0.2 – 0.4 kg/t**). Enforcement is through plant-by-plant permitting.

Canada

1990: British Columbia sets AOX limits of **1.5 kg/ADt**, to be met by 1995. Since lowered to **0.6 kg/ADt**.

1992: Quebec passes AOX limits that are phased in gradually. AOX limit of **0.8 kg/ADt** by 2000. New mills limited to **0.25 kg/ADt**.

1993: Ontario passes AOX limits that are phased in gradually. AOX limit of **0.8 kg/ADt** by 2000.

United States

1993: Proposed Cluster Rule suggests TCF as best available technology. Never took effect.

1997: Revised Cluster Rule limits monthly average AOX releases to **0.62 kg/t** pulp for existing sources, and **0.27 kg/t** pulp for new sources. Daily discharges cannot exceed 0.95 kg/ton pulp and 0.48 kg/ton pulp, respectively. Mills have until 2001 to comply.

Japan

1991: Pulp and paper industry proposes voluntary AOX limit of **1.5 kg/metric ton** by end of 1993.

2000: First law limiting dioxins in wastewater (1 pg/l). No specific limit for AOX or for the pulp and paper industry.

10. ECF-TCF Bleaching: Environmental Discussion Air

Very little to no real industrial data comparing air emissions in ECF versus TCF exists in available literature. In our opinion, we expect small reductions in volatile organic compounds in the bleaching process with TCF technology.

11. ECF-TCF Bleaching: Energy Discussion

No discussion of the energy usage in the bleach plant or the amount of energy produced was found in the literature. Our expectations are that the electrical power demand is related to the number of stages used in the bleach plant and typically the number of stages in ECF and TCF bleach plants are comparable. However, the steam usage in the bleach plant might be slightly lower for TCF because the ozone stages run at lower temperatures and do not require any additional steam. The difference is expected to be very small.

The decrease in the overall yield discussed earlier will result in higher amounts of steam generated in the recovery boiler. If the yield is 4% lower, then approximately 4% more steam will be generated in the boiler. Higher amounts of energy generated will decrease the amount of fossil fuel used in the mill. Complete process simulation will need to be developed to calculate the exact impacts.

The electrical energy for bleaching chemicals consumed in different bleaching chemicals were reported by Axegard (1993). A summary is shown in **Table 11.1**. The amount of electrical energy necessary to generate the bleaching chemicals was lower for the TCF sequence.

Table 11. 1. Electrical energy to produce bleaching chemicals for select ECF and TCF sequences.

Kappa after Oxygen	Bleaching Sequence	Electrical energy for bleaching chemicals kWh/tonne pulp
18	(CD)(EO)DED	160
18	D(EOP)DD	260
8	D(EOP)DD	150
8	QPZP	96

However, note that the sequence in **Table 11.1** does not correspond to any of those used for TCF bleaching of softwoods shown in **Table 4.1**. The QPZP sequence in Table 11.1 is not used in the existing TCF sequences in **Table 4.1** and thus is not reflective of what is actually ocurring now.

Further, an LCA approach needs to be made on all chemicals including ozone and oxygen in order to conclude differences on electricity cradle to gate.

12. Summary of ECF-TCF

TCF bleaching uses non-chlorine containing compounds whereas ECF bleaching does. There is chlorine that exists in TCF bleaching though, originating from the wood and the water and chlorinated materials are found in both TCF effluent and pulps.

Yields for TCF bleaching is less than for ECF bleaching.

TCF bleaching is more complicated and generally involves more water recycling which necessitates better process control on dissolved species in the water system.

The cost for producing softwood pulps using the TCF process is higher than that for ECF bleaching sequences because of the lower overall yield and the higher cost for the bleaching chemicals. Those can be offset to a degree by the higher amount of steam generated from the recovery boiler and the potential for the recovery of the sodium hydroxide. A single estimate found in the literature indicates TCF production costs are on the order of 5% higher than ECF. No detailed itemized costs for the overall production cost has been reported and a detailed process simulation is needed to develop a fair comparison of to estimate the overall production costs.

The pulp strength for papermaking is expected to be lower for TCF sequences at similar brightness. However no data was found on the impact on pulp quality for use in diapers or other fluff pulp applications. It may also be very costly to achieve very high brightness with the TCF bleaching sequences.

There are examples of organic chlorine content in TCF pulps that are higher and lower than for ECF pulp. In addition, levels of organic chloride in both cases are low enough that it is not a relevant factor.

The AOX in the effluent higher with ECF sequences, however no correlation was found between low levels of AOX in the paper mill effluents from ECF bleaching sequences and environmental effects. However there is not sufficient data comparing ECF and TCF bleaching sequences to make any definitive conclusions. The inorganic chlorate discharge with ECF sequences may be a factor that effects toxicity.

The total water effluent discharge from the mill can be significantly lower with TCF than ECF of the possibility that water from the bleaching process is recycled for fresh water usage in the pulping operations.

Table 12.1 summarizes the comparison of ECF versus TCF bleaching.

Table 12.1 Comparison of ECF versus TCF Bleaching

Adoption by Industry	ECF is the overwhelming technology of choice (96% of all bleached softwood world-wide and has been accepted by the EPA as the best available technology.
Technical Complexity to Implement	TCF is a more complex process to control. Issues arise when tight closure of the water loops are used to conserve water.
Chemicals Used	ECF uses chlorine dioxide for a bulk of the bleaching, an especially selective chemical that does not generate toxic chemicals. TCF uses a variety of non-chlorine chemicals that are not as selective as chlorine dioxide.
Yield on Wood	ECF has up to 4% higher yield on wood than does TCF bleaching at the same pulp properties.
Strength Properties	ECF has stronger pulps at the same brightness for papermaking applications.
Optical Properties	TCF pulps with similarly high brightness as ECF pulps can be made but suffer from lower strength properties.
Fluff Pulp Properties	No published data on TCF vs ECF pulp fibers for absorbency and wicking and other pertinent diaper applications have been found.
Cost	It is about 5% more expensive to produce TCF than ECF pulps.
Organic Halide in Pulp	Both TCF and ECF have some organic halides but in both cases the amounts are so low as not to be relevant.
Total Water Usage	TCF bleaching can cause the overall pulp and paper operations to have a greater than 50% water usage decrease relative to ECF bleaching.
AOX in water	TCF bleaching produces effluent with much lower (but not zero) AOX than does ECF.
TOC and COD in water	Depending on the mill water management, it is expected that the concentration of COD, BOD and TOC to be lower for TCF than ECF pulping because the TCF mills could be recycling bleach plant effluent to the recovery system.
Toxicity	Effluents that have been processed with secondary treatment from pulp and paper mills have the same approximately zero toxicity. No evidence of dioxin like compounds is known for ECF or TCF effluents.
Air Pollution	No data has been found in the literature. It is expected that the VOCs from bleaching for TCF will be lower.
Power Consumption for Mill Overall	Lower wood yields due to TCF bleaching would produce more dissolved wood that will produce more energy in the mill. This is predicated on the ability to direct all bleaching effluents to the recovery boiler. No real published data exists on actual practices of recycling. Primary data and a process simulation are critically needed to better explore this.
Electricity to generate chemicals	Lower for TCF than ECF for the one published source. More detailed analysis of current TCF mills is mandatory.

13. Life Cycle Analysis of Pulp and Paper

Life cycle analysis is a method to evaluate a product or process impact on the environment throughout its lifetime, considering all life cycle stages (Schenk and White, 2014). In order to conduct a LCA, an inventory of all mass and energy flows that cross the boundary of the technosphere and the environment (elementary flows) must be constructed. These elementary flows are then converted to environmental impacts through the use of models.

When considering the product of ECF pulp or TCF pulp, the collections of a consistent, accurate set of mass and energy flows in and out of a pulp mill is paramount. However, there does not exist a reliable set of consistent and current data on the existing TCF pulp mills. This is the challenge of comparing ECF with TCF pulps at this point. One approach is to simulate the pulp mill with a process model (Such as WINGems) that can compute many mass and energy flows based on process knowledge through experiments and secondary literature data.

One of the most thorough LCA studies of bleached pulp was done by AFPA in 2010, encompassing 72 North American mills and 22 million tons of printing and writing papers, about 77% of this production in 2006-2007 (AFPA, 2010). The contributions of several key stages/operations in office paper are shown in the **Table 13.1**. A ream of dry paper weighs 2.15 kg. The production phase is the most significant operation. Overall conclusions indicated that (1) paper production impacts are driven largely by fossil fuel use, (2) that the percentage of material recycled is important, (3) that avoiding landfilling by burning paper for energy was positive, and (4) transportation was not important. With regard to the overall 160 kg of used water associated with the ream of office paper life cycle, 133 kg are used at the mill for manufacturing and more than 90% of this is returned to the environment.

Table 13.1 Environmental impacts of the cradle to grave of 2.15 kg of fully bleached copy paper.

Table 2. LCIA Results
Ream of Office Paper

Impact category	Unit	Total (ream)	1. Fiber procurement	2. Uncoated freesheet production	4. Transport of UCF	5. End-of-life	Carbon storage*
Global warming	kg CO_2 eq.	4.25	8.8%	58.3%	1.4%	36.7%	-5.1%
Acidification	H^+ moles eq.	1.43	12.6%	83.5%	2.9%	0.9%	N/A
Respiratory effects	kg $PM_{2.5}$ eq.	0.00676	5.1%	93.6%	0.7%	0.6%	
Eutrophication	kg N eq.	0.00775	3.5%	38.8%	0.6%	57.2%	
Ozone depletion	kg CFC-11 eq.	2.60E-07	8%	77%	5%	11%	
Smog	kg NOx eq.	8.81E-03	26.2%	58.5%	10.9%	4.4%	
Fossil fuel depletion	MJ surplus	3.02	16.5%	78.7%	3.5%	1.2%	

*Carbon sequestration in use and landfill.

An LCA study (cradle to mill gate) of TCF pulp in Spain was conducted to identify and quantify the environmental impacts and identify operations for improvement (Gonzalez-Garcia et al, 2009). A life cycle inventory is shown in **Table 13.2**.

Table 13.2. Energy and chemicals used in forest operations (top) and global life cycle inventory data (bottom) for per ton of air dry pulp at 10% moisture content.

Table 1

Summary of energy and chemicals consumption in forest operations (S1) per 1 ton air dried (10% moisture content) of Kraft pulp.

INPUTS from TECHNOSPHERE			
Materials	**Silviculture operations**	**Logging operations**	**Secondary hauling**
Chemicals			
Fertilizer (NPK)	10.69 kg	–	–
Pesticide (glyphosate)	0.426 L	–	–
Fossil fuels			
Diesel	6.10 kg	8.14 kg	6.50 kg

Table 2

Global inventory data for Pulp mill (S2) per 1 ton air dried (10% moisture content) of Kraft pulp.

INPUTS from TECHNOSPHERE			
Materials	**Value**	**Materials**	**Value**
Biomass		Wire[a]	2.60 kg
Green Eucalyptus logs	2.70 m^3	Fossil fuels	
Wood waste	0.50 kg	Fuel oil	53.00 kg
Chemicals (100% purity)		Propane	0.40 kg
O_2	27.00 kg	**Energy**	**Value**
H_2O_2	23.00 kg	Electricity	575 kWh[b]
NaOH	14.60 kg	Steam	5.50 ton[c]
H_2SO_4	10.70 kg	**Transport**	
Na_2SO_4	7.30 kg	20–28 ton trucks	57.44 tkm
CaO	4.40 kg	Trans. freight ship	20.68 tkm
EDTA	3.00 kg		
H_2	1.90 kg		
$MgSO_4$	0.30 kg		
Anthraquinone	0.22 kg		
INPUTS from ENVIRONMENT			
Water	32.70 m^3		
OUTPUTS			
To TECHNOSPHERE		**To ENVIRONMENT**	
Materials	**Value**	**Emissions to air**[d]	**Value**
Bleached pulp (10% moisture)	1 ton AD	CO_2	212.70 kg
Energy		NO_x	1.02 kg
Electricity to grid	32.32 kWh[f]	SO_2	0.58 kg
Waste to treatment		Particulates	0.43 kg
Ashes (to landfill)	14.68 kg	TRS	0.013 kg
Dregs (to landfill)	12.85 kg	**Emissions to water**[e]	
Debris (to landfill)	1.18 kg	AOX	0.004 kg
Scrap (to landfill)	1.34 kg	COD	5.84 kg
Municipal solid waste (to landfill)	0.85 kg	BOD_5	1.44 kg
Paper and cardboard (to recycling)	39.87 g	N	0.28 kg
Glass (to recycling)	3.74 g	P	0.070 kg
		TSS	1.14 kg
		Water effluent	32.70 m^3

[a] Wire is used in the packaging step, for making the bleached pulp bales (250 kg/bale).
[b] From those only 5.82 kWh are taken from the grid and the remaining comes from cogeneration units.
[c] From biomass boilers.
[d] Direct emissions from the biomass and black liquor boilers as well as lime kiln.
[e] Direct emissions from the WWTP.
[f] Electricity surplus is sold to the national grid.

The environmental impacts were estimated using the CML 2 method and the results appear in **Figure 13.1**. It is clear that the pulp mill operations (including external productions of chemicals used) have more impact than the forestry operations. Further, chemical production and energy production dominate the impacts, **Table 13.3**. Waste treatment is important in three categories and waste water treatment plant (COD emissions) are important only in eutrophication. Chemicals such as hydrogen peroxide, sodium hydroxide and DTPA that are required in TCF bleaching are identified as having high contributions to the impacts. Unfortunately, this study does not reveal differences between ECF and TCF bleaching.

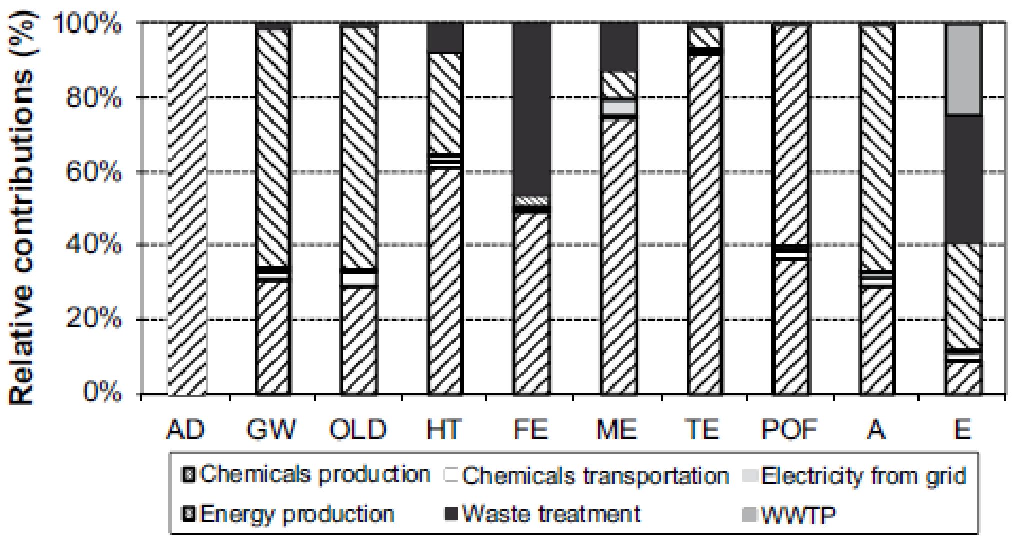
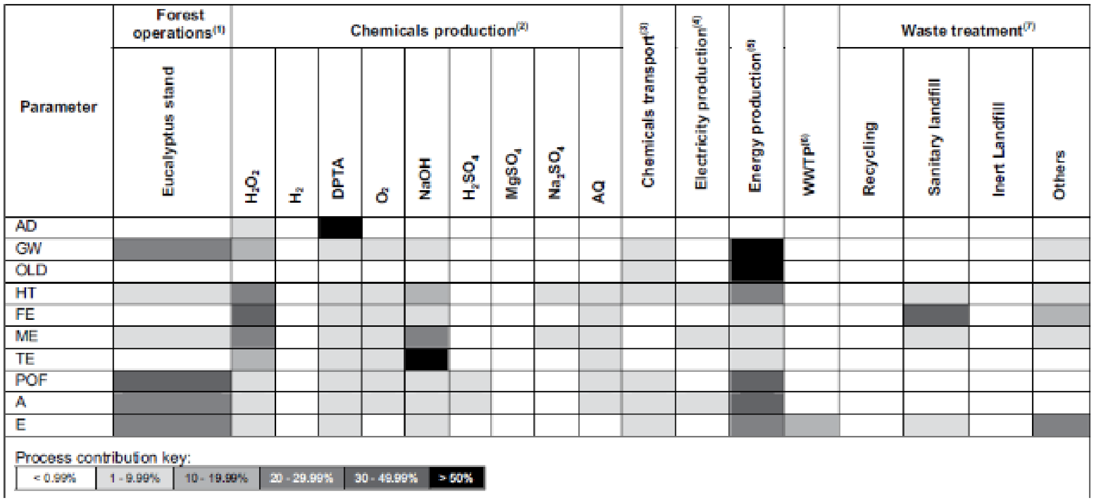


Fig. 3. Relative contributions of the different processes involved in the pulp production system.

Figure 13.1. Percent contributions of different life cycle operations to different impact categories. Life cycle operations from bottom to top of the bar: Chemical production indicated with lines rising from left to right, chemical transport is white, electricity is grey, energy production lines falling from left to right, waste treatment black and WWTP waste water treatment plant grey.

Table 13.3. Heat map of contributions to environmental impact categories.

Table 4
Contribution of processes to environmental flows.



Venditti and coworkers also did an LCA on softwood bleachable grades (Culbertson et al, 2015) and identified the generation of ClO2 in bleaching and the use of natural gas as being two of the most significant environmental drivers, **Table 13.4.**

Table 13.4. Key life cycle inventory for the production of softwood bleached kraft pulp (top) and the relative contributions, heat map, of some LCA operations on environmental impacts (bottom).

Table 5: Life Cycle Inventory Data for

Outputs	**BC**
Power & Recovery	
CO_2eq (kg/hr)	250488
SO_2eq (kg/hr)	162.7
Production	
Lignin (ADmt/hr)	0.00
Power (MWhr/hr)	71.7
SBSK Pulp (ADmt/hr)	52.5
Soap (mt/hr)	1.52
Solid Residue (mt/hr)	6.07
Inputs	
Power & Recovery	
NaOH (mt/hr)	0.22
Na_2SO_4 (mt/hr)	0.00
CaO (mt/hr)	2.52
Natural Gas (MJ/hr)	130787
Power (MWhr/hr)	63.3

Bleaching	
NaOH (mt/hr)	0.94
H_2O_2 (50%, mt/hr)	0.74
H_2SO_4 (mt/hr)	0.23
R10	
H_2SO_4 (mt/hr)	1.15
$NaClO_3$ (mt/hr)	2.26
CH_3OH (mt/hr)	0.23
Lignin Extraction	
CO_2 (mt liq/hr)	0.00
H_2SO_4 (mt liq/hr)	0.00
Natural Gas (MJ/hr)	0.00
Woodyard	
SW Feed (mt/hr)	139.4

Table 9: Relative Contribution of Process Inventory to Environmental Impact Categories. Data is based on the SOL-P scenario. Other scenarios are consistent with these results.

Total Emissions	NaOH, 50%	CaO	H_2O_2, 50%	H_2SO_4	$NaClO_3$	CH_3OH	CO_2 (gas)	NG	DE	SW	Solid Residue	Transport, Raw Matls.	Transport, Feedstock
GW	10%	6%	3%	1%	22%	0%	4%	84%	720%	-757%	0%	1%	7%
AD	4%	0%	1%	6%	8%	1%	1%	58%	1%	16%	0%	1%	4%
CG	9%	0%	4%	2%	39%	0%	3%	28%	0%	2%	11%	0%	1%
NCG	3%	0%	5%	1%	46%	1%	1%	42%	0%	1%	0%	0%	0%
RE	6%	1%	1%	7%	13%	1%	1%	63%	0%	5%	0%	0%	2%
EU	9%	1%	2%	2%	16%	0%	3%	13%	0%	14%	35%	1%	4%
OD	8%	5%	4%	1%	16%	1%	4%	43%	0%	0%	1%	2%	15%
EC	18%	1%	12%	1%	50%	0%	3%	10%	0%	3%	1%	0%	1%
SM	4%	1%	1%	1%	8%	0%	1%	21%	0%	50%	0%	2%	12%

All three of these studies are in agreement, processing chemicals and sources of energy are major drivers to the life cycle of pulp and paper products.

These studies are focused singly on either TCF or ECF processes. Due to differences in functional units, geographic locations, time periods for study, allocation methods, system boundaries, unit operations and life cycle stages, product systems, life cycle impact assessment methods and categories etc., it is unwise to compare these results to each other to make a broad claim about TCF vs ECF environmental performance.

None of the cited studies have fairly addressed the LCA differences between ECF and TCF. A literature search through Google Scholar confirms the lack of available information for this. This indicates there is a strong need for computer simulations with fair and consistent assumptions based on primary manufacturing data or secondary data from published sources are needed to compare the two systems.

A single LCA study that encompasses both bleaching processes in a consistent, robust, manner in which the two bleaching systems can be fairly compared and trade-offs identified does not exist. This type of study is critical in understanding differences between ECF and TCF bleaching.

14 Life Cycle Analysis of Diapers

With respect to diapers LCA studies, The Environment Agency in the UK (Environmental Agency, 2005, 2008), Proctor and Gamble in the US (Weisbrod and Van Hoof, 2012) and WIP in Italy (Marabella et al. 2013) have produced some of the most robust and relevant studies in the field.

The Environment Agency (2005) LCA study showed that for disposable diapers, home laundered diapers and commercially laundered prefolded cloth diapers delivered to the home in order to diaper a child for 2.5 years that none of these showed any clear environmental performance advantage in any environmental category, although the life cycle stage impacts are different. For all three systems the resource depletion, acidification and global warming were the most significant environmental impacts, **Figure 14.1.**

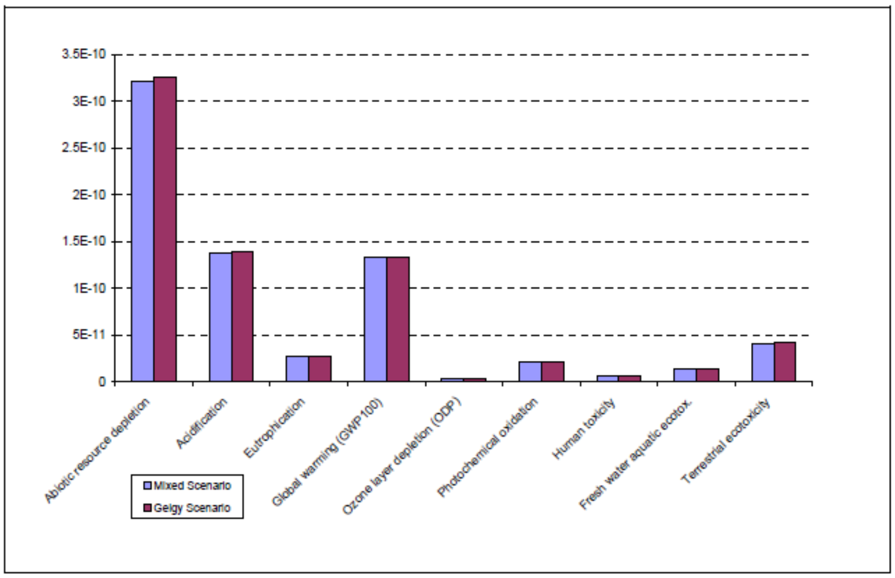


Figure 9.9 Normalisation chart for disposable nappies

The chart's scale represents the contribution of one child's use of nappies over 2.5 years to total European impacts in 1995.

Figure 14.1. Contribution of one child's disposable diaper use of 2.5 years divided by the total European impacts in the same category in 1995. The mixed and Geigy scenarios reflect different assumptions on the volume of excreta per child.

The Environment Agency (2008) analysis demonstrated the environmental effects of disposable diapers. The diaper design and manufacturing, the diaper disposal method, and the laundry choices for the shaped diapers effects on the environment were demonstrated. Some results are shown in the **Table 14.1**. It was concluded that manufacturing has a greater effect than waste management in landfill. The global warming was found to be similar for disposable diapers as for reusable diapers, 550 and 570 kg CO2e for a child in diapers for 2.5 years. It was also estimated that the reusable diaper's global warming could change by -40 to +75% based on how the diapers were laundered. This shows how sensitive the results are to process assumptions.

Table 14.1. Results of disposable diapers (top) and home-laundered reusable diaper systems that are shaped and fitted diapers with Velcro or buttons but need separate water proof outer pants.

Table 4.1 Normalised Baseline Results (Europe 1995 (EU15 plus Norway and Switzerland))

Impact category	Unit	Disposable nappy baseline*
Abiotic depletion	person year equivalents	0.115
Acidification	person year equivalents	0.047
Eutrophication	person year equivalents	0.012
Fresh water aquatic ecotoxicity	person year equivalents	0.001
Global warming potential	person year equivalents	0.044
Human toxicity	person year equivalents	0.003
Photochemical oxidation	person year equivalents	0.009

* The results compare two and a half years of nappy use with one year of emissions from an average European person.

Table 4.9 Normalised Baseline Results (Europe 1995 (EU15 plus Norway and Switzerland))

Impact category	Unit	Shaped nappy baseline
Abiotic depletion	person year equivalents	0.108
Acidification	person year equivalents	0.027
Eutrophication	person year equivalents	0.010
Fresh water aquatic ecotoxicity	person year equivalents	0.003
Global warming potential	person year equivalents	0.045
Human toxicity	person year equivalents	0.004
Photochemical oxidation	person year equivalents	0.005

* The results compare two and a half years of nappy use with one year of emissions from an average European person.

The Proctor and Gamble study (Weisbrod and Van Hoof, 2012) had as an objective to determine which factors affect the sustainability of disposable baby diapers. Product design changes from 2007 to 2010 were investigated to see their effects on environmental indicators. The functional unit was 4,623 diapers in the US or 3,796 diapers for Europe, both of which were considered to diaper a baby for its lifetime.

Nonrenewable energy, global warming potential (GWP), respiratory effects from inorganics were found to be significant environmental impacts (see **Figure 14.2**). Other indicators in the IMPACT20202+ life cycle assessment model were essentially insignificant relative to these indicators. Also, total solid waste, and cumulative energy demand (CED) were concluded to be significant (data not shown here).

Fig. 2 Normalized Impact2002 + midpoint categories for the 2010 (*green*) vs. 2007 (*red*) diapers in the USA. *Asterisks* indicate that the potential impact is associated with power generation, not directly related to product manufacture or use. The diapers have potentially relevant contributions to three of 15 environmental impact indicators estimated by this LCIA method

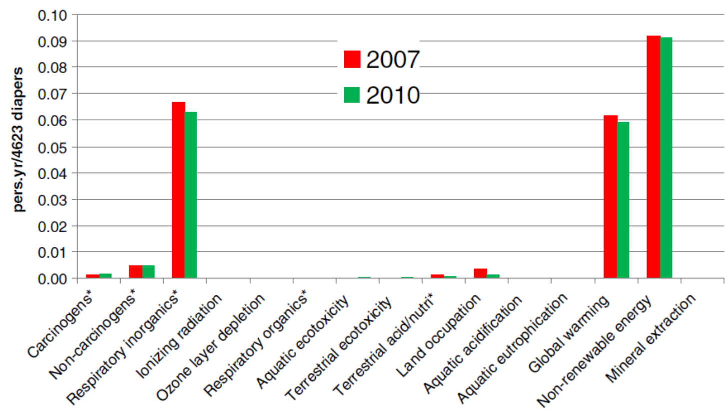


Figure 14.2. Normalized impacts of a lifetime of disposable diapers to a European person year of the environmental impact that currently exists.

Sourcing and production of diaper materials contribute most to environmental indicators, with contributions ranging from 63-92% for all impact categories, 84% of non-renewable energy and 64% of GWP (**Figure 14.3**). Of the materials, the superabsorbent and polypropylene are the primary contributors to the raw materials contribution in **Figure 14.3** (data not shown). Diaper disposal is a small contributor (1-12%). Diapers are about 1.6 and 3.0 % of landfill material in the US and Europe, respectively. Redesign of the diapers was able to reduce many impacts, with reductions mainly in the single digits, from 1-14%. No impact increased more than 10%.

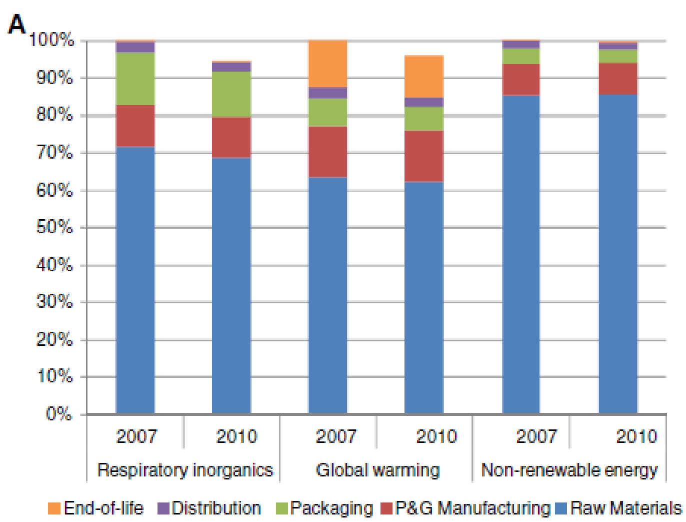


Fig. 4 Contributions to the relevant midpoint categories for the 2007 and 2010 diapers in a the USA with 4,623 diapers and **b** Western Europe with 3,796 diapers. Results are normalized to the 2007 total scores of all life cycle phases for each indicator

Figure 14.3. LCA unit operations contributions to the overall impact categories deemed significant.

While the Proctor and Gamble study did not address TCF vs ECF pulps and its impact on the LCA, the company has issued a statement (P&G, 2015) on these pulps, *As a company, we only purchase pulp bleached by the ECF and TCF bleaching processes since various studies have validated that these methods being safe in terms of dioxin formation. To ensure that ECF and TCF methods produce safe pulp for use in sanitary product like diapers, follow-up studies were conducted to validate that the pulp manufacturing plants that replaced elemental chlorine gas bleaching with ECF or TCF bleaching and show no signs of dioxin being present in pulp, emissions, or in fish downstream from the plant* (Hamm and Göttsching, 2002).

The study in Italy (Mirabella et al, 2013) evaluated using biopolymers instead of petrochemical plastics and the use of renewable energy in the overall LCA cradle to gate of diapers. Contributional analysis indicated that sourcing and the production of raw materials contributed most significantly to potential environmental impacts, **Figure 14.4.** In 16 of 18 environmental categories wood pulp was reported to be responsible for greater than 20% of the environmental impact. Super absorbent material was also a significant source of environmental impact. Diapers with a new design and biobased plastics had improved environmental impact *only* in 11 of 18 categories. For normalized environmental environmental impact categories, the new design and biobased plastics diaper had a significant decrease in three of the four categories that had greater contributions than the other 14 environmental impact categories. Suggestions for diaper environmental improvements included better selection of material suppliers, shorter transportation distances along supply chain, and composting of the diapers at end of life.

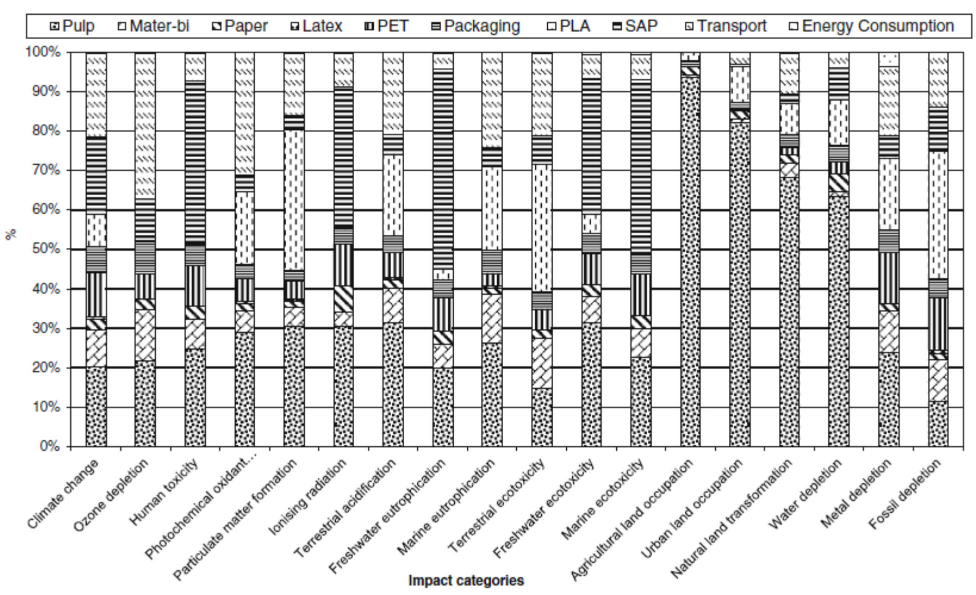


Fig. 3 Results of characterization stage (LCIA method ReCiPe 2008) related to the functional unit of 1 diaper. "Others" represents the raw materials whose overall contribution is less than 4 %

Figure 14.4. Contributional analysis of operations to the overall impact categories. Notice that pulp is a significant contributor in almost all categories.

A review of these LCA studies indicates that there does not exist an environmental LCA that considers the impact of using TCF versus ECF in the overall environmental performance of a diaper. Existing studies utilize ECF pulps (it is assumed and this should be checked). The LCA studies indicate that raw materials are an important contributor to overall environmental impacts but there needs to be a detailed investigation of the contribution of pulp to the overall raw materials category.

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