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An Investigation into the Environmental and Chemical Aspect of Sugarcane Paper and Wood Fiber

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An Investigation into the Environmental and Chemical Aspect of Sugarcane Paper and Wood Fiber Paper



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Abstract

The University of British Columbia is a leader in the sustainability movement. With the increasing demand for paper in the developing countries such as China and India, the growing concerns for the environmental impacts are expected to accumulate over time. Our report investigates the environmental concerns in the production stages of both types of paper. The investigation focuses on various categories such as chemicals used in bleaching, different types of bleaching processes, quantitative analysis on wastewater, and alternative methods of bleaching process. This report includes a case study in Iran, academic journals, and data collected from past production reports. Based on the findings from the investigation, it is environmentally prominent to opt for bagasse (sugar cane) paper when it is challenged with wood fiber paper due to the quantity of wastes generated, and the amount of water required to effectively treat the said wastes.

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Figure 1: Water used, and the generated wastewater (K. Ranganathan, 2007)

Glossary

Alkaline condition – The pH value has to high than 7.

Bagasse – Fiber material that remains after sugarcane juice is being extracted.

Bleaching – Chemical process that decrease the color of the pulp or bagasse.

Dioxin – A diverse range of chemical compounds which are known to exhibit dioxin-like toxicity

Elemental Chlorine Free (ECF) – A technique that is using the chlorine dioxide for bleaching.

Environmental Protection Agency (EPA) -an agency created for protecting human health and the environment by enforcing regulations and laws passed by Congress
 Lignin – Complex chemical compound that is taken out from wood.

Total Chlorine Free (TCF) – A technique that is complete not using any chlorine chemical for bleaching.

COD- The standard method for indirect measurement of the amount of pollution (that cannot be oxidized biologically) in a sample of water.

BOD- The amount of oxygen required by aerobic microorganisms to decompose the organic matter in a sample of water, such as that polluted by sewage. It is used as a measure of the degree of water pollution.

AOX- refers to a family of stable compounds produced when halogens (for example, chlorine) are used for bleaching, such as chlorine, bromine, and iodine, react with organic matter

TSS- A measure of the suspended solids in waste water, effluent, or water bodies.

List of abbreviations

AOX-Adsorbable Organic Halides

C – Chloride

COD- Chemical Oxygen Demand

BOD-Biochemical Oxygen Demand

D - Chloride dioxide

E - Extraction with sodium hypochlorite

ECF -Elemental chlorine free

ECT – Elemental Chlorine Free

EPA- Environmental Protection Agency

H - Sodium Hypochlorite

O – Oxygen

P - Alkaline Hydrogen peroxide

PAA - Peroxy acids

PCF -Processed Chlorine Free

TCF – Total Chlorine Free

TCF- Totally chlorine free

TSS- Total Suspended Solids

X-Enzymes

Y - Sodium hydrosulfite

Z – Ozone

1.0 Introduction

The world demand for paper is expected to grow 2.1% by 2020. Due to this increase of demand, the growing concern over the environmental effect of paper mills is expected to increase, as well. Moreover, the increase cost of pulpwood and the constraints of fiber supply in the paper industry have led to the development of competitive alternatives to the wood fiber paper. One of these alternatives is sugarcane paper, or bagasse paper. Processes of producing paper are similar in all types of fiber raw materials ¹³. The differences, if existent, only arise due to the availability of different process options for each section of the paper mills. This paper investigates the environmental effects caused by producing paper from wood, or sugar cane and compares the effects of both in order to provides the more environmentally cleaner option.

2.0 Chemical use for Bleaching

After researching, we found out that the chemical uses for bleaching process are not quite different from the sugarcane paper and wood fiber paper. The purpose of the bleaching process is to decrease the color of the pulp from the wood fiber or sugar cane bagasse. The brightness and whiteness is very important to make papers, therefore the bleaching process are necessary for such purpose. However the chemical that is used in the bleaching process has a great negative impact on the environmental.

2.1 Bleaching Chemical

The most common chemical use in a bleaching process are, Chloride with letter C, Sodium Hypochlorite with letter H, Chloride dioxide with letter D, Extraction with sodium hypochlorite with letter E, Oxygen with letter O, Alkaline Hydrogen peroxide with letter P, Ozone with letter Z, Enzymes with letter X, Peroxy acids with letter PAA, and Sodium hydrosulfite with letter Y. Different bleaching methods uses different chemical to bleach. For example the bleaching sequence CEHEH has an effect of exposing the pulp to chlorine, and "extract with the a sodium hydroxide solution to remove lignin fragmented by the chlorination, treated with sodium hypochlorite, washed with sodium hydroxide again and given a final treatment with hypochlorite".

Chlorine dioxide is used alone in the elemental chlorine-free (ECF) bleaching sequence, but the chlorine dioxide usually is used combining the chlorine. The reason for using the chlorine dioxide is to "minimize the amount of organochlorine compounds produced" (E.Sjostrom,1993). Chlorine dioxide is the most common use round the world. However chlorine dioxide is very explosive and unstable in high concentration. Therefore this chemical is used immediately after it is been produced.

In order to produce the chlorine dioxide, sodium chlorate needs to react with sulfur dioxide.

2 NaClO₃ + H₂SO₄ + SO₂
$$\rightarrow$$
 2 ClO₂ + 2 NaHSO₄ (E.Sjostrom,1993)

Chloride is also the most common used chemical in bleaching process. The reason is that the characteristic of strong electrophilic and oxidizing. The principle is to remove the lignin from the cellulose fibers, though "aromatic substitution"

The chloride reacts with water will replace hydrogen atom on the "aromatic rings of lignin" with chloride atom and hypochlorous acid.

$$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HClO$$

(Fari, G.M.;J.C. Morris, S.L. Chang, I. Weil, and R.P. Burden,1948)

All the bleaching chemicals that are used to de-lignify are going to smaller and oxygen-container molecules. These breakdown materials need to be removed, before these chemicals react again, from the bleaching process. These chemicals are easily removed because the materials are soluble in water.

Since the chemical chloride has negative impact to the environment, a total chlorine free bleach process has been discovered, TCF. Ozone is the additional method of bleaching sequence to chloride dioxide, and not using any ECF. The benefit of using the ozone in the bleaching process is to decrease the use of other chemical in the bleaching process, so that to decrease the negative impact to the environment from the waste of using the chemical. The disadvantages of ozone bleaching are that the ozone has a very low water solubility, which means that the disposal of the ozone waste would be a

problem, and the ozone is toxic even in a very low level. During the bleaching process, ozone will "reach with the carbon carbon double bonds in lignin, including those within aromatic rings", ("the original", 2007) and the cleaved aromatic rings form muconic acid.

Hydrogen peroxide requires many dynamic conditions for removing the lignin. The hydrogen peroxide is firstly being degraded to superoxide and hydroxide radicals, and which would remove the lignin. The pH value and the temperature for this chemical reaction are very high. The pH value requires to be larger than 9, and the temperature needs to be larger than 90 degree Celsius. Before using the hydrogen peroxide, chelating agents is used to remove the metals that would decompose hydrogen peroxide. Compare to Chloride or Chloride dioxide, hydrogen peroxide is less selective under the lignin removal condition.

Another chemical that is used in bleaching, which produces less chlorinated organic to waste is Oxygen. The cost of oxygen is much lower than chlorine dioxide, resulting many paper manufactory choose oxygen over chlorine dioxide. Also the oxygen has lower corrosiveness than the other chemicals. On the other hand, there are many disadvantage of oxygen bleaching. Using oxygen bleaching can only remove fifty percent of lignin; the process will lose selectivity after removing fifty percent of lignin in order to improve the selectivity of oxygen bleaching, magnesium can be added for that purpose. The oxygen has very low water solubility therefore the treatment for the waste would be very expensive. Because the oxygen is used in the bleaching process as a gas, therefore the oxygen is not very reactive. And in order for it to react with ionized phenolic hydroxyl group, the beaching process has to carry out under alkaline condition.

3.0 Bleaching process

Woodchips are raw material for producing wood pulp. They are produced by woodchipper, which are machines powered by internal combustion engine ranging from three to a thousand horsepower. After woodchips are made by cutting larger pieces of wood, they are graded and the leftover woodchips are to be used as a solid fuel for heating in buildings or in energy plants for generating electricity.

The raw material is not naturally white; the appearance of pure whiteness is a result of multi-phase bleach processes. Wood comprises of lignin and cellulose; Cellulose is the structural component for making pulp and paper, and lignin is a natural adhesive that binds wood fibers together. During the pulping process, the lignin and cellulose are separated, and up to about 90 percent of the lignin are dissolved without degrading the cellulose fiber (Reeve, 1987).

The objective of removing lignin from the pulp is to lighten the color of the pulp, ensure paper remains brighter longer, and improve quality (Gerholdt, 2007, para. 3). The pulp is bleached in a combination of alternating bleaching and washing phases, the pulp can be very bright without degrading its structure and strength. When the last of the lignin is removed from the pulp after repetitive bleaching processes, the chemicals used in bleaching effectively dissolve any extractives contained in the pulp and dissolves remaining bark debris.

3.1 Bleaching methods

Chlorine is the most commonly used whitening agent for bleaching. There are three common methods of bleaching processes: elemental chlorine-free (ECF), processed chlorine-free (PCF), and totally chlorine-free (TCF) (Gerholdt, 2007, para. 4).

3.1.1 Elemental chlorine-free

The most common method used in North American pulp mills is Elemental Chlorine Free bleaching because it is due to mandates put on pulp mills by US EPA ¹ regulation to eliminate the use of elemental chlorine gas (Gleason,2009). However, "ECF does not preclude the use of chlorine compound and derivatives of chlorine, such as chlorine dioxide" (Gerholdt, 2007, para. 5). ECF only reduces the potential of dioxin², carcinogens and toxic compound formation; they are disposed from pulp mill's waste water to waterways, affecting the aquatic ecosystem.

3.1.2 Total chlorine-free

Total Chlorine-free bleaching does not use any chlorine chemicals; it utilizes Hydrogen peroxide, oxygen and ozone promoting a zero-discharge system where all possible solid and liquid waste is recycled. Ozone removes residual lignin from pulp more effectively than peroxide, but the ozone requires special equipment. However, the quality of the paper is competitive to chlorine bleached paper (Gleason, 2009).

3.1.3 Processed chlorine-free

Recycled papers are typically processed by chlorine-free method. Typical chemicals used include peroxide, oxygen and hydrosulfite, but no chlorine or derivatives are used in the process. The quality of these papers is often compatible to TCF or ECF paper.

² Dioxin is extremely harmful to the environment and human health

¹ Environmental Protection Agency (EPA)

3.2 Cost of different methods

Chlorine free bleaching methods are more cost beneficial than elemental chlorine because chlorine free can result in costs savings in pollution control, safety equipment, security and workplace safety costs (Gerholdt, 2007, para.14). Paper mills are not adopting these environmentally and socially preferable bleaching alternative is because the capital cost in investment can be substantial, but in the long term these mills will save money (Environment America, 2007).

In 2000, Samoa mill is the first mill in the world that operates on total chlorine free process, which required an additional of \$7.2million. However, the long term benefits are: "2% increase in pulp production, 12% reduction in total mill waste, including a 31% reduction in bleach plant effluent, and a 19% decrease in water use"; this lowers the mill's operating cost by \$1.1 million (Environment America, 2007).

4.0 Alternative Bleaching Technology

The main environmental concerns of the paper production are dioxin level in both air and water wastes, and the organic load of Adsorbable Organic Halides (AOX). These concerns arise mainly from the bleaching process¹³. Due to the increase demand and pressure to reduce the emission and release of those compounds, research has been focused in obtaining the most environmentally process available.

4.1 Adsorbable Organic Halides (AOX)

Adsorbable Organic Halides are a family of chemicals produced from halogens, such as chlorine, reaction with organic materials. AOX has a unique property of adsorption on activated carbon. Although the introduction of AOX is a recent subject of research, the effect on marine life and aquatic environment is well documented. In fact, AOX has been reported as carcinogenic chemical.

4.2 Alternative Methods of Bleaching

Dioxin and AOX arise from the use of chlorine gas, and chlorine dioxide as bleaching agents in the bleaching process. Chlorine use has been decreasing rapidly in the industry and substituted with chlorine dioxide¹⁴. No bleaching substitute to chlorine dioxide, with the same potential has been found. However, research has been focusing on other ways to eliminate the problems of both AOX and dioxin levels. Due to the fact that each wood or bagasse fiber differs in content that any other same fiber, bleaching requirements, in terms of amounts, differ. In other words, each fiber used in every industry is unique and requires different amounts of bleaching than other fibers, although not substantially different³. Thus, in order to reduce AOX and dioxin levels, experimental data on different bleaching sequences are done for different plants in literature¹³. In India, an analysis was made that recorded a reduction in AOX content by 10-65% by adhering to a certain bleaching sequence that uses chlorine dioxide¹³.

4.3 Case Study in Iran

A case study in Iran was conducted to investigate the Pars paper factory in Iran. The plant is 1500 km from Tehran, the capital city. Hafttapeh Sugarcane Factory, which is the supplier of the raw materials of the paper plant, is near the Pars factory. This analysis of the plant included a life cycle analysis of sugarcane paper. The government of Iran owns the Pars Paper Factory. It has a production capacity of 40,000 metric tonnes of paper produced solely from bagasse.

One of the conclusions of the study is that energy and water consumption, Chlorine and raw materials used, and Greenhouse Gases emitted are less for sugarcane paper than in virgin wood paper. In other words, producing one tonne of paper from bagasse can save 17 trees, 360L of water, 100L of gasoline, 60 pounds of air pollutants, 10401 kilowatts of electricity, and 3.3 cubic meter of landfill space (Poopak & Reza, 2012).

5.0 Environmental Assessment of Waste Water

Waste water that is streamed down from large hard-wood paper mills and sugarcane (bagasse) mills contain very high levels of BOD and COD contents, toxic substances, acids, and recalcitrant organics (organic and synthetic). Exposure to these wastes has been known to cause or can result in carcinogenic, Endocrine disruptor, diarrhea, intense vomiting, nausea, eye irritation, respiratory stress, oxidative stress and liver damage. These wastes carry life-threatening risks to the locals around the factory and for the organisms that live in nearby lakes and rivers.

5.0.1 Where Are These Wastes Coming From?

Paper machine waste water is generated from large factory mills, where shredded wood or bagasse is cooked with white liquor, and bleaching units, where the partially-organic pulp is treated with chemicals such as chlorine dioxide. About 40-45% of the raw materials for paper are recovered as cellulose fibers, and the remaining parts are discharged as waste water (Ranganathan, 2007), which contains organic compounds and pulp fiber. These organic compounds are referred to as BOD, COD, Adsorbable Organic Halides (AOX), and Total Suspended Solids (TSS).

5.0.2 COD and BOD?

Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are indirect measurements of the quantity of organic material in a sample of waste water. COD refers to the amount of water required (mg/L) to break down an organic compound by converting it to carbon dioxide, ammonia, and water through oxidation. Similarly, BOD refers to the amount of water required (mg/L) for biological organisms in a body of sample water to break down the organic material within a specific temperature and time period.

5.0.3 AOX Content

AOX refers to a family of stable compounds produced when halogens (for example, chlorine) are used for bleaching, such as chlorine, bromine, and iodine, react with organic matter. AOX has a unique property of adsorption on activated carbon. Although the introduction of AOX is a recent subject of research, the effect on marine life and aquatic environment is well documented. AOX compounds are reported to be carcinogenic and bio-accumulative, and cause "chronic toxicity in aquatic organisms when they are discharged in large quantities as waste water." (Ranganathan, 2007).

5.1 Water Consumption for Diluting Water Wastes

After bleaching process and the actual paper manufacturing process, there is a large quantity of "black liquor" released. This is the embodiment of COD and BOD content. To remove a substantial amount of COD and BOD, large quantity of water is used to dilute the solution. The distilled water help to stabilize and help remove as much COD and BOD as possible. The problem is the amount of water used in the diluting process; for this process to effectively remove contaminated waste water, substantial amount of water is used.

Industry	Raw material used	Current production (t d ⁻¹)	Bleaching steps	Water required (m ³ d ⁻¹)	Wastewate generation (m ³ d ⁻¹)
Paper industry unit-I	Hard wood (>90%) and WP	520 (90)	С-ЕР-Н-Н	71,820	64,200
Paper industry unit-II	Hard wood and bamboo (80%), IP	330 (30)	С-ЕР-Н-Н	35,600	33,540
Paper industry unit-III	Hard wood and bamboo	299	C/D-EP-Do-E-D1	38,500	34,455
Paper industry unit-IV	Hard wood and bamboo, (>90%), IP and WP	295 (50)	O-Do-EOP-D1	55,000	38,000
Paper industry unit-V	Paddy straw, bagasse and WP	80 (20)	C-E-H-H	11,000	7,894
Paper industry unit-VI	Paddy straw and WP	30 (10)	C-E-H/ C-H-H	3,000	2,150
Paper industry unit-VII	Rice straw, kraft pulp and WP	135 (70)	C-E-H	10,500	8,450
Paper industry unit-VIII	WP	70	H	3,200	2,700
Textile bleaching-I	Cloth	0.40	H	34	32
Textile bleaching-I	Cloth	0.70	H	34	32.00
Textile bleaching and dyeing unit-III	Cloth	0.42	P	17.5	17

Figure 1: Water used, and the generated wastewater

In the figure above, it is important to note that the waste water generated through the process is 87~93% of the actual distilled water used. For one ton of paper, 250 m³ of water is used for the production. The amount of waste water pollution generated through the paper production is very large. In comparison to wood fiber paper, the production of bagasse paper requires less water, and generates less waste water as a result.

5.2 Possibility of Alternative Methods for Bleaching?

The main environmental concerns of the paper production are dioxin level in both air and water wastes, and the organic load of Adsorbable Organic Halides (AOX). These concerns arise mainly from the bleaching process13. Due to the increase demand and pressure to reduce the emission and release of those compounds, research has been focused in obtaining the most environmentally process available.

Dioxin and AOX arise from the use of chlorine gas, and chlorine dioxide as bleaching agents in the bleaching process. Chlorine use has been decreasing rapidly in the industry and substituted with chlorine dioxide14. No bleaching substitute to chlorine dioxide, with the same potential has been found. However, research has been focusing on other ways to eliminate the problems of both AOX and dioxin levels. Due to the fact that each wood or bagasse fiber differs in content that any other same fiber, bleaching requirements, in terms of amounts, differ. In other words, each fiber used in every industry is unique and requires different amounts of bleaching than other fibers, although not substantially different3. Thus, in order to reduce AOX and dioxin levels, experimental data on different bleaching sequences are done for different plants in literature13. In India, an analysis was made that recorded a reduction in AOX content by 10-65% by adhering to a certain bleaching sequence that uses chlorine dioxide13.

6.0 Conclusions and Recommendation

Although bagasse and wood paper production have similar processes, the investigation of the environmental effect of bagasse and wood paper production has yielded that bagasse, in general, have less environmental effects that wood paper. Nevertheless, this analysis resulted from excluding transportation effects as well as using recycled wood in the production of wood-based paper. It is recommended that a life cycle analysis to be done that focuses on a specific plant with specific customers.

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