



ENERGY FROM BIOMASS IN PULP AND PAPER MILLS

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Abstract

Pulp and paper mills generate various quantities of energy-rich biomass as wastes, depending on technological level, pulp and paper grades and wood quality. These wastes are produced in all stages of the process: wood preparation, pulp and paper manufacture, chemical recovery, recycled paper processing, waste water treatment. Energy recovery from wastes of different origin has become a generally accepted alternative to their disposal. Pulp and paper industry expresses an interest in adapting and integrating advanced biomass energy conversion technologies into its mill operations. Industrial adoption of these new technologies has the potential for higher efficiency, lower capital cost, and safer operation than conventional operations that burn fossil fuels for energy. Incineration with energy recovery has the advantage of hygienic disposal, volume reduction, and the recovery of thermal energy by means of steam or super heated water that can be used for heating and power generation.

The paper reviews the current state and tendencies in using as a fuel of solid wastes generated in pulp and paper mills. A description of biomass-derived wastes regarding their opportunity to be used for energy recovery is presented. The heating properties of wood wastes, rejects from recycled paper processing, paper sludge, and low-quality recovered paper grades are discussed. Some aspects of emission of greenhouse gases (GHG) are also presented.

Key words: air emissions, biomass incineration, environment, pulp and paper, solid wastes

1. Introduction

According to the requirements of the Kyoto Protocol, the European Union must accomplish over the period 2008-2012 an overall greenhouse gas emission reduction by 8% compared with the 1990 levels. A realistic option is represented by substitution of typical fossil fuels with low-carbon fuels for energy production purposes. Energy recovery from wastes of different origin, e.g. industrial or agricultural, has become moreover a generally accepted alternative to their disposal or incineration. Waste-to-energy is gaining more and more attention as landfill costs and environmental concern increase and, at the same time, space available for landfilling waste is diminishing, especially in densely populated areas. Along with landfill, CO₂ and CH₄ emissions, potential groundwater pollution, the reduction of space available for landfilling has led to policy and legislation to increase the recycling and reuse of wastes. Legislation under preparation in the EU will prohibit landfilling of energy-containing waste.

Biomass is defined as any organic material derived from plants. Biomass is produced through photosynthesis as plants convert the sun's energy into

chemical energy. The chemical energy in biomass can be extracted through combustion to produce energy that can be used as heat or power. Sustainable managed biomass resources are considered green because they are renewable and do not contribute to global warming. Carbon dioxide generated from the combustion of biomass is consumed as plants regrow, so that as long as the resource is sustainable managed (for example, through replanting), the net contribution of carbon dioxide to the atmosphere is zero. Biomass represents an attractive source both for energy recovery and for valuable chemicals obtaining, (Popa and Volf, 2008).

Pulp and paper industry's role in the national bio-energy production is significant in many European countries. In 2004 the bio-energy accounted for 638.8 PJ (15.3 Mtoe) in pulp and paper industry in Europe, which represents 50% of the total energy consumption in pulp and paper industry. Pulp and paper industry accounts on average 27% of bio-energy use in these countries and 23% of total bio-energy use in EU countries. Renewable energy share in pulp and paper industry has increased from 45.5 % (1996) to 54.5 % (2006), (CEPI, 2007). Pulp and paper industry is an energy-intensive but energy-efficient industry. Energy can represent up to 40% of

manufacturing costs. Many pulp and paper mills generate more than half of their energy needs from biomass fuels recovered from solid waste and process streams (Table 1). Energy-rich biomass, derived from black liquor, wood chips, bark, sawdust, rejects, sludge, is the result of atmospheric carbon dioxide amassed by trees during growth and transformed into organic carbon substances. Carbon dioxide emissions from biomass combustion are not counted in the GHG inventory.

Table 1. Shares of energy carriers in total energy consumption in the member countries of the Confederation of European Paper Industry, (CEPI, 2007).

<i>Fossil and non-fossil fuels</i>	<i>Share, %</i>
Biomass (black liquor is included)	50
Gas	34
Oil	9
Coal	5
Other fossil	1
Other	1

2. Biomass in pulp and paper industry

Biomass resources include agricultural residues, wood wastes from forestry and industry, residues from food and paper industries, municipal green wastes, sewage sludge, dedicated energy crops such as short-rotation (3-15 years), coppice (eucalyptus, poplar, willow), grasses, sugar crops (sugar cane, beet, sorghum), starch-containing crops (corn, wheat) and oil crops (soy, sunflower, oilseed rape). Organic wastes and residues have been the major biomass sources so far, but green energy is gaining importance and market share in the last decade. With re-planting, biomass combustion is a carbon-neutral process as the CO₂ emitted has previously been absorbed by the plants. Residues and wastes are mostly used for heat and power generation. Sugar, starch and oil crops are primarily used for fuel production.

The pulp and paper industry has adapted and integrated advanced biomass energy conversion technologies. Industrial adoption of these new technologies has the potential for higher efficiency, lower capital cost, and safer operation than conventional operations that burn fossil fuels (Bowyer and all, 2005). A list of biomass generated in pulp and paper industry is presented in Table 2. The characteristics of typical fuels are listed in Table 3.

Black liquor is the most important biomass fuel in a kraft pulp mill. Black liquor contains around 50 % from wood substance as dissolved organic fraction. Typical higher heating values for black liquor lie between 13,000 and 15,500 kJ/kg of solid black liquor, depending on wood species and pulp yield. Burning of black liquor in a special recovery boiler generates around 4 tones of steam per tone of pulp. By processing of steam in a back-pressure turbine, a high quantity of electricity is produced. Recovery boiler covers the steam and electrical

energy consumption of the pulp mill (Adams and Frederik, 1988).

Elemental composition of black liquor solids and typical values for heating value are presented in Table 4 (Krotscheck and Sixta, 2006).

Table 2. Biomass wastes in pulp and paper industry.

<i>Type of biomass</i>	<i>Sources of biomass wastes</i>
Black liquor	Chemical pulp manufacture (kraft process)
Bark and wood residues	Chemical and semi-chemical pulp processes and mechanical pulp manufacture
Rejects of screening and cleaning processes	Chemical pulp production; recycled paper processing; paper stock preparing
Mechanical-chemical sludge	White water treatment and effluent treatment
Biological sludge	Biological effluent treatment
Deinking sludge	De-inking of recycled paper
Mixed sludge	Different sources

3. Wood wastes as a fuel

The source of wood wastes in a pulp mill is the preparation of pulpwood. The wood wastes generate in a pulp mill are: sawdust coming from the slasher deck, bark falling from the debarking drum, pins and fines from chip screening, wood residue from wood-yard. The characteristics of wood wastes are as follows:

- wood wastes consist of particles with various dimensions and shapes (from sawdust to log butts);
- moisture content of wood wastes is high and time depending;
- heating value of wood wastes is highly influenced by their moisture content;
- generation of wood wastes in the pulp mill is time-depending

Bark represents up to 300 kg/t of pulp and shares 60-90 % from wood wastes in a pulp mill (Gavrilescu, 2004). Its properties are:

- bark particles are very different regarding their dimensions (1 to 100 mm or larger) and shapes;
- bark moisture content is high and depends on debarking method: dry debarking leads to 40-50 % bark moisture while semi-wet debarking leads to 70-80 % bark humidity;
- bark particles are rigid and brittle;
- bark can absorb water easily, which is difficult to eliminate;
- ash content of bark is much higher than of wood;
- heat of combustion is around 20,000 kJ/kg (dry basis); the moisture drastically reduces heating value of bark.

Pins and fines are generated at the logs chipping: The percentage of pins and fines in chips depends on: pulpwood quality, short-or long-wood receiving, wood species, chipper performance.

Table 3. Comparison of typical fuel properties, (Clarke and Guidotti, 1995)

<i>Heat value and components</i>		<i>Bark</i>	<i>Mech. & biological sludge</i>	<i>Deinking sludge</i>	<i>Peat</i>	<i>Coal</i>
Heat value – as received, kJ/Kg, (at average moisture)		5900 (60%)	4200 (63%)	2800 (58%)	9200 (50%)	24000 (12%)
Ash (dry basis),%		3	20	50	5	14
Elemental analysis (dry basis), %	C	50.6	33.7	19.0	57.1	71.6
	H	5.9	4.4	2.4	6.2	4.9
	S	-	0.3	0.05	0.2	0.6
	N	0.5	0.7	1.0	1.9	1.9
	O	40.2	41.2	27.4	29.6	7.0

Table 4. Chemical analysis and heating values of black liquor solids

<i>Component, % on dry solids</i>	<i>Wood species</i>	
	<i>Hardwood</i>	<i>Softwood</i>
C	33.5	37.0
H	3.7	3.9
N	0.1	0.1
O	35.8	34.0
S	4.4	3.7
Na	19.9	19.2
K	1.5	1.5
Cl	0.5	0.5
Higher heating value, MJ/Kg	13.2	15.1

Pins and fines represent 50-100 kg/t o.d. pulp and their main characteristics are:

- pins are small wood pieces, while fines contains both wood and bark particles;
- bark content ranged between 20-50 %;
- particles dimension is optimum for firing;
- moisture level (40-50 %) of this fraction allow to their combustion without dewatering

Wood wastes generated in a pulp mill are listed in Table 5.

Table 5. Wood wastes generated in a pulp mill

Wood wastes	Quantity, kg/t of o.d. pulp
1. Sawdust coming from the slasher deck	10-30 kg/ t of pulp
2. Bark falling from the debarking drum	100-300 kg/t of pulp
3. Pins and fines from chip screening	50-100 kg/ t of pulp
4. Wood waste from wood yard	0-20 kg/t of pulp
Total:	160 – 450 kg/ t of pulp

The most common way to use wood residues is to burn it for heat (Huhtinen, 2000). The economic importance of the wood wastes depends both on its heating value and moisture content. High moisture content is detrimental in two ways (Lyngfelt and Leckner, 1999):

- reduces the available heat of wood wastes;
- reduces boiler efficiency, because heat energy is lost in vaporizing the moisture in wood and bark.

The influence of spruce bark moisture on the available heat is presented in Table 6.

Table 6. Available heat versus moisture content for spruce bark

<i>Moisture content (percent)*</i>	<i>Available heat, kJ/kg</i>
0	20, 000
10	16, 300
30	12, 000
50	8, 100
70	4, 400

*most furnaces operate poorly if moisture content exceeds 50 %

In order to burning, wood wastes must be screened to remove oversized pieces, and pressing or dried, (if necessary) to reduce their moisture content at minimum as possible, 50 % or lower. Wood-waste is a medium heating value fuel, the average heating value being 20,000 kJ/kg (dry basis). The acceptable lower limit of the heating value ranges from 7,500-8,000 kJ/Kg corresponding to around 50 % wood-waste moisture, (EBIPPC, 2001; Koch, 1985). In order to enhance the boiler efficiency, fossil fuels (coal, oil, natural gas) are co-fired with wood wastes. The ratio of fossil fuel/wood wastes of 30/70 (heat input basis) is considered as acceptable. Wood-waste burning allows obtaining 0.8-2.0 t steam (1.2 MPa)/t of o.d. pulp, depending on wood losses at pulpwood preparation and boiler performance (Fogelholm, 2000). Solid residues from wood waste combustion are ash and incompletely combusted carbon. Combustion of hogged fuel generates 40-100 kg ash/t of pulp (Koch, 1985). The ash content of the wood, bark and wood wastes are listed in Table 7 and the emissions from combustion of hogged fuel are presented in Table 8 (Gavrilescu, 2005).

Table 7. Ash content of wood and bark

<i>Material</i>	<i>Ash content (percent)</i>
Wood	0.7-2.0
Bark	4-6
Wood wastes (as hogged fuel*)	5-8

*sand and dirt are included

Rejects are generated during chemical pulp treatment and recycled paper processing. The two categories substantially differ regarding their properties and use in the pulp and paper mill. Rejects generated at chemical pulp treatment are represented by "knots" (coarse screening of pulp) and rejects (fine screening of pulp), (Kostinen, 2000; Ljokkoi, 2000). "Knots" is a general term that includes: true knots from wood, uncooked chips and bark particles. Knots represent 2-6 % on unscreened pulp or 25-70 Kg/t of pulp and their characteristics are:

- various size (5 to 50 mm) and shape;
- knots are dense and rigid;
- knots are impregnated with black liquor moisture content 70-80%)

This fraction may also contain small rocks, metal pieces, wires etc.

Table 8. Emissions from combustion of hogged fuel, mass percent (example)*

<i>Gases</i>		<i>Particulate matter</i>	
Nitrogen	65	Inorganic fly ash	
Carbon dioxide	8	Fixed carbon	
Oxygen	11	Traces of salts and metals	
Water vapor	12		

96-98 % of total			
Carbon mono-oxide	0.1		2-3 % of total
Unburned hydrocarbons			
0.005			
Sulfur dioxide			
0.01			
Oxides of nitrogen			
0.005			

*no fossil fuels are used

Knots processing methods are: knots cooking (in a separate digester) or mixing them with fresh chips; knots refining (when the knots are free from black liquor); knots burning (after mixing with wood wastes); knots landfilling. Burning of knots is not a common method for their processing in a pulp mill. Fine screening rejects contain fiber bundles and the common practice is refining and subsequent screening. In some cases, fine rejects are separated from circuit and mixed with knots.

4. Rejects from recycled paper processing

Depending on the final product, the reject rate varies from 5 % e.g. for used corrugated containers to 25 % and even more for waste graphical papers. Based on a final rejects dryness of 60 %, their amount lies from 83 kg to 416 kg per ton of paper. Reject is non-homogenous. The two major categories are coarse and fine rejects. Coarse reject has its origin in recovered paper pulping and de-trashing, as well as coarse screening. Fine reject comes from process stages like cleaning, fine screening and from the approach flow.

There are heavy coarse rejects like metal of all kind, shape and size; stones, not disintegrated

paper or wet strength paper, wires, etc. Light coarse rejects consist from fiber bundles, plastics pieces, foils, polystyrene, etc.

Fine rejects differentiate into light and heavy weight. Heavy fine rejects mainly consist from sand, glass, staples and other metallic office waste, discharged from cleaners, as well as from the heavy junk traps of combined screening/cleaning equipment. Light fine rejects from slot screening or light weight cleaning contain fiber broke, spin-ups, stickies, wax, filler etc. Low-organic content rejects (non-combustible heavy rejects) are landfilled.

The portion of the reject which is suitable for incineration (light coarse rejects) has to be discharged at the highest possible dryness, accompanied by the highest possible caloric value (> 11 MJ/Kg). It might be even necessary to apply a drying process in order to achieve the above-mentioned limit of the calorific value. Furthermore, the particle size of the rejects has to meet the requirements of the available incineration technology. The content of organic contaminants in the non-burnable, inorganic fraction has to be limited to a minimum, in order to allow disposal, (Ronga and Brauer, 2004).

The rejects from the pulping of recycled paper contain large quantities of plastics that range between 20 and 60 Kg/t depending on recycled paper grade. Plastics are "engineered" materials made by combining polymers with additives that build its desired properties such as mechanical resistance, flexibility, extruding/molding capacity, flame resistance, color, etc. Most polymers contain carbon and hydrogen only and their combustion products are carbon dioxide and water vapor. Some polymers contain chlorine or nitrogen and their combustion products include hydrochloric acid or hydrogen cyanide, respectively. Plastics are valuable fuel regarding available heat, as is shown in Table 9.

Table 9. Available heat and air consumption at combustion of plastics

<i>Waste component</i>	<i>Available heat, kJ/kg</i>	<i>Air consumption, kg air/kg waste</i>
Cellulosic fibers	16,000	4
Polyethylene	44,000	16
Polystyrene	38,000	13
Polyurethane	26,000	9
Polyvinylchloride	23,000	8

Combustion of plastics is a complex process and it is highly pollutant. During combination of oxygen with plastics carbon is converted to carbon dioxide, hydrogen to water, sulfur to sulfur dioxide, nitrogen to cyanides or molecular nitrogen, and chlorine to hydrochloric acid. Since most plastics are composed of carbon and hydrogen, the majority of the gases produced are carbon dioxide and water vapor. However, plastics and almost all other fuels are never burned under ideal conditions and products of incomplete combustion (PICs) may be formed that

are toxic to humans or harmful to the environment. PICs are formed because of inadequate oxygen concentration and temperatures in all areas of the furnace.

If there is inadequate mixing, complete combustion may not occur and materials are removed from the furnace and cool before they are converted into their most stable products. The PICs resulting from plastics combustion are mostly hydrocarbons, having the characteristics of the monomers from which they are made (Lyons and Kerstetter, 1990)

5. Paper sludge as a fuel

The option to use paper sludge as a bio-waste fuel for energy production has been recently considered in many European countries. The organic fraction in paper sludge is renewable, and therefore it does not contribute to net CO₂ emissions. A few mills incinerate paper sludge in their boilers as “hog” fuel. This practice is not widespread, because the heating value is very low (Table 3) and the high moisture of the sludge affects its ability to burn efficiently. To enhance the heating value, the sludge is mixed with dryer waste materials (such as wood residue). Fluidized bed combustion is an emerging technology that works particularly well with the wet sludge produced by de-inking mills. In this process, air is bubbled through a bed of inert material (usually sand or limestone), which greatly improves the combustion process. This technology also produces fewer sulfur dioxide and nitrous oxide emissions than do conventional hog boilers. Burning sludge is advantageous because the landfill volume required for ash disposal is about 25 percent of that required for sludge. In addition, boiler ash from de-inking sludge incineration is sometimes used as an aggregate in cement and concrete.

Sludge ash concentrates heavy metals, however, and if their concentration arises hazardous levels, the ash requires special handling, (Shin et al., 2005; Usherson, 1992). Every tone of recovered fiber generates up to 200 kg (dry weight) of sludge of different types and up to 400 kg (dry weight) of rejects and sludge, Table 10 shows the amount of rejects and sludge depending on the recovered paper grades and paper produced (Scott et al., 1995).

De-inking sludge consist of printing inks (black and colored pigments), fillers and coating pigments, fibers, fiber fines, and adhesive components. More than 55 % of the solids removed by flotation are inorganic compounds. They are primarily fillers and coating pigments such as clay and calcium carbonate. The proportion of cellulosic fiber is low. The heating value depends on the ash content and is 4.7–8.6 GJ/t of dry substance, (Hamm, 2006). The sulfur, fluorine, chlorine, bromine, and iodine contents are low and for this reason, no costly flue gas purification systems are necessary when incinerating de-inking sludge. Compared with sludge from biological effluent treatment plants, the nitrogen and phosphorus contents are very low. This is something that requires consideration when using de-inking sludge for composting and agricultural and land application purposes. The level of heavy metals in sludge of recovered paper processing is generally low. Sludge of de-inking plants contains less contamination than those of municipal wastewater treatment. The concentration of cadmium and mercury is especially insignificant and sometimes even below the detection limit of the test method applied (atomic absorption spectrometry). Only the concentration of copper has the same order of magnitude as that of municipal sewage sludge. The copper content of deinking sludge is primarily due to blue pigments of printing inks which contain phthalocyno- compounds (Kiphann, 2001).

Table 10. Amount of rejects and sludge depending on the recovered paper grades and paper produced

Paper grade	Recovered paper grade	Wastes (% by dry mass)				
		Total	Rejects		Sludges	
		Rejects and sludges	Heavy-mass and coarse	Light-mass and fine	Flotation de-inking	White water clarification
Graphic paper	News, magazines	15-20	1-2	3-5	8-13	3-5
	High grades	10-25	< 1	≤ 3	7-16	1-5
Sanitary paper	News, magazines, office paper, medium grades	27-45	1-2	3-5	8-13	15-25
Market DIP	Office paper	32-46	< 1	4-5	12-15	15-25
Liner, fluting	Old corrugated containers, Kraft papers	4-9	1-2	3-6	-	0-1
Board	Sorted mixed recovered paper, Old corrugated containers	4-9	1-2	3-6	-	0-1

Halogenated organic compounds such as polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDD), and polychlorinated dibenzofurans (PCDF) are found in the flue gas. The PCB concentration is below 0.3 mg/kg dry solids (0.3 ppm) and PCDD/PCDF concentrations of deinking sludge show a similar pattern of decline. Due to the change from elemental chlorine bleaching of chemical pulp to oxygen delignification and chlorine dioxide bleaching, the PCDD/PCDF contents of deinking sludge have been decreasing significantly.

Today, PCDD/PCDF concentrations of deinking sludge are 25–60 ng I-TE/kg dry solids (I-TE - International toxicity equivalent). PCDD/PCDF concentrations are not significantly higher than the average contents of PCDD/PCDF in municipal sewage sludge. As a result of modifications of the bleaching sequences in chemical pulping, dioxin formation does not occur in most pulp producing countries. Consequently, dioxin discharges from recovered paper processing mills are already low and will decrease further (Hamm, 2006).

Regarding dewatering capacity, a distinction has to be made between de-inking sludge and the primary (chemical) and secondary (biological) sludge of the waste water treatment. This sludge contains ink particles, adhesives from the converting processes, mineral fillers such as clay, calcium carbonate, and some cellulosic fibers. The dewatering capacity of deinked sludge is low. By contrast, the sludge from paper mill waste-water treatment plants, which contains higher percent of cellulosic fibers is much easier to dewater than de-inking sludge. It can be stated that the higher the fiber content, the higher the dry substance content that can then be obtained through dewatering. Sludge handling methods are available for all types of sludge produced by the common effluent treatment processes. De-inking sludge is usually handled mixed with the effluent sludge. Maximum mechanical dewatering of sludge prior to incineration is essential, (EEA, 2006).

Due to its low heating value, sludge must be co-fired with fuels having higher heating value, as bark and wood residues, see Table 3. Problems of sludge utilization for co-firing with bark have been reported as (Usherson, 1992):

- low heating value of all types of sludge which limits the ratio of sludge at boiler feeding;
- too much water in the sludge gives difficulties in keeping the boiler load;
- too big amount of sludge at boiler feeding may sinter in the fuel bed or in the ash handling system;
- limitation in capacity of ash handling systems;
- increasing environmental problems associated with sludge combustion due to the presence of toxic metals.

All types of sludge contain toxic trace metals (Pb, Cd, Cu, Zn, Hg) in various quantities. The behavior of toxic trace metals in de-inking and biological sludge, has been found to be strongly affected by metal interactions with the solid substrate

in the furnace (mostly with the Al/Si structure) which acted as a limit to their vaporization. It was observed that, during fluidized bed incineration of sludge from biological treatment, the ash was formed of loosely agglomerated particles and solid fused spheres. Cd and Pb encapsulation within a Si-Al-Ca based glassy structure was also observed. Paper sludge is also characterized by high chlorine content, which will be partly retained in the fly ash as condensed alkali chlorides, the rest forming HCl to a high extent. Ash-forming constituents of paper sludge influence chlorine enrichment in fine fly ash. Kaolin enhances HCl release in the flue gas, while calcium carbonate enhances chlorine capture on the coarse fly ash fraction (Coda, 2004).

6. Recovered paper as a fuel

With the continuing increase of world paper consumption, more and more waste paper of poor or unknown quality is entering in the solid wastes circuit. Sources of waste paper fibers (secondary fibers) are as follows: mixed (varied paper quality, boxboard cuttings and mill wrappings); news (old newspapers, over-issue news, and ground wood and container plant cuttings); pulp substitutes (grades of white colored kraft, white and semi-bleached sheets/cuttings, tab cards, trims and unprinted grades); purchased de-inked (de-inked white and colored ledger, computer printout, ground wood, coated book and bleached sulfate sheet and cuttings); other (lightweight coated grades). For this part of the waste paper stream, a better solution (other than fiber recovery) is its incineration. Although these residues are still largely dumped on landfill sites, a trend towards thermal processing is considered.

Mixed recycled paper represents a valuable source of energy for several reasons: it is easy to separate from the waste stream; it is relatively homogeneous and mostly free from metals, putrescibles and other noncombustible materials; it requires minimum processing to be converted into densified form of energy suitable for direct combustion; its heating value is fairly high; it has a low sulfur content, and low nitrogen oxides (NO_x) emissions. One tone of wastepaper combusted as fuel will produce 9.8 GJ of thermal energy (Porteous, 2007). Table 11 shows the calorific values of some paper grades.

Table 11. Calorific values of some paper grades

<i>Paper grade</i>	<i>Mean gross calorific value, kJ/kg (dry basis)</i>
Newspaper	17,600
Kraft and cardboard	16,100
Boxboard	16,000
Tissue	15,200
Office paper	14,700

The moisture content of mixed paper waste lies between 6-28 % by mass. If the moisture content

do not exceeds 20 %, heating values of mixed paper waste samples do not show big differences. Moisture contents exceeding 30 % lead to low heating value for mixed paper waste and must also be detrimental for shredding and for pelletizing of mixed paper waste.

During paper combustion all carbon in the organics is converted to carbon dioxide, with a trace amount of carbon monoxide. Hydrogen is converted into water vapor, and all chlorine is converted into hydrogen chloride, HCl, and chlorine gas, Cl₂. Sulfur is converted to sulfur dioxide, SO₂ and sulfur trioxide, SO₃. Nitrogen is converted into nitrogen oxides such as nitrogen monoxide, NO, or nitrogen dioxide, NO₂, and nitrogen gas, N₂. Organics are decomposed into lower molecular mass species at high temperature in the flame zone. When some of these smaller species meet with oxygen and hydroxyl radicals, some combustion intermediates such as aldehydes, ketones, alcohols, and acids are formed. In incomplete combustion, further oxidation of these intermediates is hindered due to flame quenching by cold air, water, or by a cold surface, or lack of additional oxygen. Therefore these intermediates are emitted from the flame zone as PICs (Lyons and Kerstetter, 1990).

Typical emissions that can be expected from the combustion of mixed paper waste are particulates, carbon dioxide, carbon monoxide, water, oxygen, nitrogen, oxides of sulfur, oxides of nitrogen, ammonia, hydrocarbons as hexane or methane, aldehydes as formaldehyde, and organic acids as acetic acid. Primary air pollution concern is with emission of particulate matter rather than gases and odors. A big portion of particulate emission arises from the carry-over of mineral matter introduced with paper waste.

The quantity of particulate emissions from an incinerator depends on the waste composition and the design and operation of the incinerator. Mixed paper waste, like all solid wastes and fuels, has substantial ash content. Some amount of the fly ash may settle in the bottom of the furnace or in other sections.

Settlement reduces the emission rate depending on the settling rate which is related to the size and mass of fly ash particles, flue gas properties, and residence time in the furnace. The ash content of paper waste is a major factor influencing the particulate emission rates, and the amount of ash carried over generally ranges between 10-20 % of the total, (Lyons and Kerstetter, 1990).

Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste includes the limit values for incineration plant emissions (EC Directive, 2000). They concern heavy metals, dioxins and furans, carbon monoxide (CO), dust, total organic carbon (TOC), hydrogen chloride (HCl), hydrogen fluoride (HF), sulfur dioxide (SO₂), nitrogen monoxide (NO) and nitrogen dioxide (NO₂). The limits are listed in Table 12.

7. Greenhouse gas emissions

The Kyoto Protocol set very ambitious targets for reducing energy consumption and emission of greenhouse gases (GHG). Emissions included in the inventory were as follows:

- carbon dioxide emission from fossil fuel combustion that includes those from production processes, as well as from the use of company-owned vehicles and from other equipments producing CO₂. Emissions are estimated using widely-accepted emission factors, which are based on the carbon content of the fuel;
- methane and nitrous oxide emissions from combustion processes, which are estimated using emission factors. Emissions of CH₄ and N₂O are usually very small compared to those of CO₂, and some inventory protocols do not address such emissions;
- greenhouse gas emissions from mill landfills and wastes water treatment plants, which are estimated using mill-generated data, and are consistent with methods suggested by the Intergovernmental Panel on Climate Change (IPCC).

Table 12. Air emission limit values at solid waste incineration, (EC Directive, 2000).

<i>Pollutant</i>	<i>Concentration, mg/Nm³ at 11 % oxygen</i>
Total dust	10
VOC as C	10
HCl	10
HF	1
SO _x	50
NO _x	200
Cd	0.05
Hg	0.05
Heavy metals, total	0.5

In 2001, the International Council of Forest and Paper Associations (ICFPA) began a project to develop an international methodology for estimating GHG emissions. The calculation tools were recognized by governments as well as by domestic and international organizations, establishing protocols and developing calculation techniques as the appropriate tools for calculating GHG emissions for pulp and paper mills, (ICFPA, 2002; NCASI, 2005). Although emission of CO₂ from biomass burning is almost excluded from GHG inventories, methane (CH₄) and nitrous oxide (N₂O) from biomass burning are included. If a company has reliable site-specific data allowing it to estimate CH₄ and N₂O emissions from biomass combustion, it should use this data. Otherwise, it will be necessary to use the most appropriate emission factors available. Unfortunately, there are little data on CH₄ and N₂O emissions from biomass boilers and recovery furnaces (Table 13).

The table summarizes the available information on methane and nitrous oxide emissions from biomass-burning boilers. The variability in the data reflects the many different types and ages of boilers, diversity of operating conditions, control equipment and fuel characteristics.

Where an emission factor description shown in Table 13 matches the conditions at a mill, the company may want to select that emission factor for estimating mill emission.

In many cases, however, because of the ranges in emission factors and the limited ability to match emission factors to boiler design, operating conditions and fuels at this time, it is reasonable to use the average emission factors shown in Table 13.

Table 13. Emission factors for CH₄ and N₂O from biomass combustion, (NCASI, 2002, NCASI, 2005)

Combustion unit	Emission factor description	CH ₄ kg/TJ	N ₂ O kg/TJ
Wood wastes fired boilers	Wood, wood wastes	30	4
	Uncontrolled emissions from wood-fired stoker boilers	15	-
	Average from wood residue combustion	9.5 ^{a)}	5.9 ^{a)}
	Average from circulating fluidized bed boilers (CFB) burning peat or bark	4	8.8
	Average from bubbling fluidized bed boilers (BFB) burning peat or bark	2 ^{b)}	< 2
	Pre-1980 wood residue-fired stoker boilers sampled ahead of control devices	8.2 ^{a)}	-
	Pre-1980 wood residue-fired stoker boilers sampled after wet scrubber	2.7 ^{a)}	-
	Wood fired boilers	41 ^{c)}	3.1 ^{c)}
	Wood as fuel	24 ^{d)}	3.4 ^{d)}
	Wood waste	30	5
	Average emission factor for wood waste	12	4
	Data dispersion of emission factors	1-40	1.4-75
Recovery furnaces	Recovery furnaces	< 1	< 1
	Recovery furnaces-black liquor	2.5 ^{d)}	-
	Black liquor	30	5
	Average emission factor for black liquor	2.5	2.0
	Data dispersion of emission factors	1-17.7	1-21.4

a) - converted from GCV to NCV assuming a 5% difference, GCV - gross calorific value, NCV - net calorific value, NCV=0.95xGCV; b) - excludes one very high number associated with low oxygen-high carbon monoxide conditions; c) - based on the heat content of 20 GJ/t dry solids, d) - based on the liquor heat content of 13.3 GJ/t dry solids

The most severe air pollution problems are usually associated with black liquor burning. Recovery boiler is a potential source of sulfur dioxide, but the emission level is generally below the accepted level. The major sources of TRS emission are digester blow and relief gases and multiple effect evaporation plant. Over the last two decades, evaporator and recovery boiler manufacturers have improved their designs to achieve higher solids liquor for firing and better mixing within the combustion zone. These improvements provide to reduce TRS emissions (Tarnawski, 2004).

Relatively little attention has been directed toward the control of nitrogen oxides, which are by-products of high-temperature combustion processes. However, both NO and NO₂ are known to have a photochemical impact on the atmosphere. Fortunately, with respect to recovery boilers and lime kilns, it appears that the formation of nitrogen oxides can be adequately controlled by operating these combustion units with a minimum flame temperature and limited excess air.

The development of fluidized-bed combustion technology seems to have very good perspectives for using low-quality fuel such as bark and other wood wastes. This kind of biomass has a relatively low content of sulfur (< 0.1%), and SO₂ emission during its combustion is much lower than in the case of coal combustion (IPCC, 2006; Matthes, 2004).

At the present, the use of biomass as a fuel, replacing fossil fuels, was demonstrated to be technically feasible and economically attractive. Benefits are gained from the reduction of plant fuel cost although the high capital costs involved. Of course, the economics of biomass energy generation should become more attractive as traditional fuel prices should increase. Other benefits are the pollutant emission reduction and the fuel self-sufficiency in self-generating fuel. The encouraging results obtained in pulp and paper mills can motivate other industries to consider the scenario of using biomass for energy.

8. Conclusions

1. In pulp and paper industry energy-rich biomass is represented by pulping liquors, wood wastes, sludge and rejects. Many pulp and paper mills produce more than half of their energy needs from biomass fuels recovered from solid wastes. Carbon dioxide emission from biomass combustion is not counted in the GHG inventory.

2. Black liquor is the most important biomass fuel in a kraft pulp mill. Black liquor contains around 50 % from wood substance. Burning of black liquor in a special recovery boiler covers the steam and electrical energy consumption of the pulp mill.

3. Wood wastes are the second biomass fuel as importance in a pulp mill. Combined wood waste and sludge generated at the mill are insufficient for

combustion demand, because of low heating value resulting from their high moisture and ash content. In order to enhance the boiler efficiency, fossil fuels (coal, oil, natural gas) are co-fired with wood wastes.

4. Rejects from recycled paper processing contain large quantity of combustible materials as plastics and cellulosic fibers. Plastics that contain only carbon, hydrogen, and oxygen are unlikely to present an environmental risk if they are burned in small quantities in well designed combustors. These types of plastics include polyethylene, polypropylene, and polystyrene. Plastics that contain halogenated compounds such as polyvinylchloride or teflon are best kept out of combustors unless there are adequate pollution control devices to handle the acid compounds that are formed.

5. The use of paper sludge as a bio-waste fuel for energy production has been recently considered in several pulp and paper mills. Due to its low heating value, sludge must be co-fired with fuels having higher heating value, as bark and wood residues. Sludge co-firing is not widespread, because its heating value is very low and the high moisture of the sludge affects its capacity to burn efficiently.

6. Low-quality recycled paper represents a valuable source of energy for many reasons: it is easy to separate from the waste stream; it is relatively homogeneous and mostly free from noncombustible materials; it requires minimum processing to be incinerated; its heating value is fairly high; it has low sulfur content, and low nitrogen oxides emissions. Pulp and paper mills show an increased interest in this topic.

7. GHG emissions from biomass incineration contain carbon dioxide, CO₂, methane, CH₄ and nitrous oxide, N₂O. The last two are usually very small compared to CO₂, and some inventory protocols do not include them. Emissions are estimated by using widely accepted factors which are based on the carbon content of the fuel. Other important gas emissions in the pulp and paper industry include SO₂, H₂S, NO_x, TRS and CO, generated in lime kiln and recovery boiler. Bark combustion produces SO₂, NO₂ and CO in small quantities.

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