Chapter 2
Emissions from Pulping

2.1 Kraft Pulping

Kraft pulping involves the cooking of wood chips at high temperature and pressure in white liquor, which is a solution of sodium sulphide and sodium hydroxide (Smook 1992; Biermann 1996; Adams et al. 1997). The white liquor dissolves the lignin that binds the cellulose fibres together. Two types of digester systems—batch and continuous—are used for kraft pulping. Most kraft pulping is done in batch digesters, although the more recent installations are of continuous digesters (Gullichsen 2000). In the batch digester, after completion of the cooking, the contents of the digester are transferred to an atmospheric tank usually referred to as a blow tank. The total contents of the blow tank are sent to pulp washers, where the spent cooking liquor is separated from the pulp. The pulp then proceeds through washing, which is done in various stages. The pulp is then bleached, pressed and dried into the finished product. The 'blow' of the digester does not apply to continuous digester systems. The balance of the kraft process is designed to recover the cooking chemicals and heat. Spent cooking liquor and the pulp wash water are combined to form a weak black liquor which is concentrated in a multiple-effect evaporator system to about 55 % solids. Then it is concentrated to 65 % solids in a direct-contact evaporator by bringing the liquor into contact with the flue gases from the recovery furnace, or in an indirect-contact concentrator. The strong black liquor is then fired in a recovery furnace (Bajpai 2008; Smook 1992). Combustion of the black liquor provides heat which is used for producing process steam and also for converting sodium sulphate to sodium sulphide. Inorganic chemicals present in the black liquor are collected as a molten smelt at the bottom of the furnace. The smelt is dissolved in water to produce green liquor, which is transferred to a causticizing tank. In the causticizing tank, calcium oxide is added to convert the solution back to white liquor for return to the digester system. From the causticizing tank, lime mud is precipitated, which is calcined in a lime kiln to regenerate calcium oxide (Adams et al. 1997). For process heating, for driving equipment, for providing electric power, etc., many mills need more steam than can be provided by the recovery furnace alone. So, conventional industrial boilers that burn natural gas, coal, oil, bark and wood are most commonly used.

The problem of kraft mill odour originating from the sulphide in the white liquor in the initial pulping has long been an environmental and public relations issue for the pulp and paper industry (Smook 1992; Springer and Courtney 1993). The kraft mill odour is caused predominantly by malodourous reduced sulphur compounds, or total reduced sulphur (TRS), namely, methyl mercaptan, dimethyl sulphide and dimethyl disulphide and hydrogen sulphide. Methyl mercaptan, dimethyl sulphide and dimethyl disulphide are the main volatile organic sulphur compounds and are formed in the pulping process, while hydrogen sulphide is formed in the recovery furnaces (US EPA 1973, 1976, 1986, 1993a, b, 2001; Das and Jain 2004; Pinkerton 1993, 1998, 2000a, b; Bordado and Gomes 1997, 2003; Someshwar and Pinkerton 1992; Anderson 1970). Reduction of odourous gas emissions in kraft mills will significantly improve the environmental competitiveness of the pulp and paper industry, and will also improve public relations with their respective surrounding communities. When it is more economically feasible, odour reduction, instead of odour elimination, can improve significantly the air quality and the environment of a kraft mill, since it will reduce the radius of the area being impacted by the odour emission.

Although significant reduction of TRS emission has been achieved in the pulp and paper industry in the last decade with advanced odour abatement technologies, subjective odour nuisance at very low concentrations still causes odour problems in the communities surrounding kraft mills. TRS formation in kraft pulping was studied as early as the 1950s, 1960s, and 1970s (Kringstad et al. 1972; Tormund and Teder 1987; Zhao and Zhu 2004; Wag et al. 1995; Frederick et al. 1996; Tarpey 1995; Zhang et al. 1999). Much of this research effort has been devoted to quantification and kinetics (Wag et al. 1995; Frederick et al. 1996; Tarpey 1995) of the organic sulphur compound formation. The general formation mechanism of the TRS has been described by Frederick et al. (1996) and Jarvensivu et al. (1997). The formation of methyl mercaptan and dimethyl sulphide is through the reaction of mercaptide ion and the methoxyl groups present in the pulping liquor (Wag et al. 1995; Tarpey 1995). Dimethyl disulphide is not formed in the pulping process; rather it is formed through the oxidation of methyl mercaptan when black liquor is in contact with air (Wag et al. 1995; Frederick et al. 1996; Tarpey 1995). Hydrogen sulphide is not formed in the normal pulping pH conditions, but rather in the downstream processes where the pH of the streams are reduced below 10 through its dissociation from sodium sulphide (Zhao and Zhu 2004; Frederick et al. 1996). Other significant sources of hydrogen sulphide formation are lime mud reburning, black liquor pyrolysis, and molten smelt dissolution processes (Zhao and Zhu 2004; Wag et al. 1995; Frederick et al. 1996).

Typical characteristics of the gaseous emissions from kraft pulp mill are shown in Table 2.1. Overall, the three most important source of odour production are black liquor combustion, weak black liquor concentration and the digestion process. It can be seen that the source of the largest volume of potential emissions is the recovery furnace, followed closely by the digester blow gases and the washer hood vents. But, the most concentrated emissions come from the digester blow and relief gases. About 0.1–0.4 kg of TRS is emitted per ton of pulp at 5 ppm in the recovery

Table 2.1 Typical offgas characteristics of kraft pulp mill. (Based on data from Andersson et al. 1973; US EPA 1973)

Emission source	Offgas flow rate (m³/ton pulp)	Concentration (ppm by volume)			
		H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3
Digester batch					
Blow gases	3–6000	0–1000	0–10,000	100–45,000	10–10,000
Relief gases	0.3–100	0–2000	10–5000	100–60,000	100–60,000
Digester, continuous	0.6–6	10–300	500–10,000	1500–7500	500–3000
Washer hood vent	1500–6000	0–5	0–5	0–15	0–3
Washer seal tank	300–1000	0–2	10–50	10–700	1–150
Evaporator hotwell	0.3–12	600–9000	300–3000	500–5000	500–6000
BLO tower exhaust	500–1500	0–10	0–25	10–500	2–95
Recovery furnace	6–000–12,000	(after direct-contact evaporator)			
		0–1500	0–200	0–100	2–95
Smelt dissolving tank	500–1000	0–75	0–2	0–4	0–3
Lime kiln exhaust	1000–1600	0–250	0–100	0–50	0–20
Lime slacker vent	12–30	0–20	0–1	0–1	0–1

Table 2.2 Odour threshold concentration of TRS pollutants. (Based on data from Springer and Courtney 1993)

Reduced sulphur compound	Odour threshold concentration (ppb)
Hydrogen sulphide (H_2S)	8–20
Methyl mercaptan (CH_3SH)	2.4
Dimethyl sulphide (CH_3SCH_3)	1.2
Dimethyl disulphide (CH_3SSCH_3)	15.5

boiler flue gases. The main difficulty with TRS emission is their nauseous odour, which are detected by the human nose at very low concentrations. The odour threshold (odour detectable by 50% of the subjects) concentrations of the principal TRS compounds emitted by kraft mills, which are only few parts per billion by volume (Springer and Courtney 1993) are shown in Table 2.2. TRS is more of a nuisance than a serious health hazard at low concentrations. Thus, odour control is one of the main air pollution problems in a kraft mill.

Oxides of both sulphur and nitrogen are also emitted in varying quantities from a few points in the kraft system. The main source of sulphur dioxide emission is the recovery furnace due to the presence of sulphur in the spent liquor used as a fuel. Sulphur trioxide is sometimes emitted when fuel oil is used as an auxiliary fuel. The lime kiln and smelt dissolving tank also emit some sulphur dioxide. The emission of nitrogen oxides is more general because nitric oxide is formed whenever oxygen and nitrogen, which are both present in air, are exposed to high temperatures. A small part of the nitric oxide formed may further oxidize to nitrogen dioxide. These two compounds, nitric oxide and nitrogen dioxide, are termed the total oxide of nitrogen. Under normal operating conditions, the temperature in the recovery furnace is not high enough to form large quantities of oxides of nitrogen (NO_x). The main source of NO_x emissions is the lime kiln. SO_x and NO_x emission rates from various kraft mill sources are shown in Table 2.3. Due to the variations in operating conditions at different mills, there are large variations in the emission rates. Large

Table 2.3 Typical emissions of SO$_x$ and NO$_x$ from kraft pulp mill combustion sources. (Based on data from US EPA 1973; Someshwar 1989)

Emission source	Concentration (ppm by volume)			Emission rate (kg/ton[a])		
	SO$_2$	SO$_3$	NO$_x$ (as NO$_2$)	SO$_2$	SO$_3$	NO$_x$ (as NO$_2$)
Recovery furnace						
No auxiliary fuel	0–1200	0–100	10–70	0–40	0–4	0.7–5
Auxiliary fuel added	0–1500	0–150	50–400	0–50	0–6	1.2–10
Lime kiln exhaust	0–200	–	100–260	0–1.4	–	10–25
Smelt-dissolving tank	0–100	–	–	0–0.2	–	–
Power boiler	–	–	161–232	–	–	5–10[b]

[a] kg/t of air-dried pulp
[b] kg/t of oil

amount of NO$_x$ are generated when the flame temperature is above 1300 °C and oxygen concentration is higher than 2 %. Modern recovery boilers should have SO$_x$ emissions below 100 ppm when properly operated. Sulphur emissions from power boilers are controlled by using fuels of low sulphur content.

Another type of odourous emissions of non-sulphur compounds is generated by the hydrocarbons associated with the extractive components of wood, such as terpenes and fatty and resin acids, and also from materials used in processing and converting operations, like defoamers, pitch control agents, bleach plant chemicals, etc. Compared to TRS emissions, these hydrocarbon emissions are small, but they may be odourous, or act as liquid aerosol carriers contaminated with TRS, or undergo photochemical reactions.

2.2   Emissions from Neutral Sulphite Semi-Chemical (NSSC) Pulping

The semi-chemical pulping process uses a combination of chemical and mechanical energy to extract pulp fibres. Wood chips are first partially softened in a digester with chemicals, steam and heat. After the chips are softened, mechanical methods complete the pulping process. After digestion, the pulp is washed to remove cooking liquor chemicals and organic compounds dissolved from the wood chips. Then this virgin pulp is mixed with 20–35 % recovered fibre or repulped secondary fibre to enhance machinability. The chemical portion of the pulping process—cooking liquors, process equipment—and the pulp washing steps are very similar to the kraft and sulphite processes. Presently in the mills, the chemical portion of the semi-chemical pulping process uses either a non-sulphur or neutral sulphite semi-chemical (NSSC) process (Biermann 1996). The NSSC process uses a sodium-based sulphite cooking liquor and the non-sulphur process uses either sodium carbonate only or mixtures of sodium carbonate and sodium hydroxide for cooking the wood chips (EPA 2001a, b).

Generally, the emissions from NSSC are much lower in comparison to those from the kraft process. As no sodium sulphide is present in the pulping liquor, both

methyl mercaptan and dimethyl sulphide are absent from the gaseous emissions, a very low amount of reduced sulphur is emitted (Dallons 1979). The sulphur emissions from the sodium carbonate (sulphur-free) process has been traced to sulphur in the fuel oil and process water streams used. The emissions of sulphur dioxide and NO_x are similar to those of a kraft mill.

2.3   Emissions from Sulphite Pulping

The cooking liquor in the sulphite pulping process is an acidic mixture of sulphurous acid and bisulphite ion (Smook 1992). In preparing sulphite cooking liquors, cooled sulphur dioxide gas is absorbed in water containing one of four chemical bases—magnesium, ammonia, sodium or calcium. This process uses the acid solution in the cooking liquor to degrade the lignin bonds between wood fibres. Sulphite pulps can be bleached more easily and have less colour than kraft pulps, but are not as strong as kraft pulps. The efficiency and effectiveness of the sulphite process is also dependent on the type of raw material and the absence of bark. For these reasons, the use of sulphite pulping is not very common and has reduced significantly in comparison to kraft pulping over time (EPA 2001a, b).

The sulphite process mainly operates with acidic sulphur dioxide solutions and as a result sulphur dioxide is the principal emission. Organic reduced sulphur (RS) compounds are not produced if proper conditions are maintained in the process. Because the odour threshold is about 1000 times higher for sulphur dioxide than for RS compounds, sulphite mills generally do not face the odour problem of a kraft mill. Volatile compounds such as methyl mercaptan and dimethyl sulphide are not produced in sulphite pulping. The method of attack on lignin by sulphite liquor is quite different than that by kraft liquor. The sulphite process involves sulphonation, acid hydrolysis and acid condensation reactions (Rydholm 1965).

Typical emissions in the sulphite process are sulphur dioxide with special oxides of nitrogen (problems arising in the ammonium-base process). Sulphur dioxide is also emitted during sulphite liquor preparation and recovery. Very little sulphur dioxide emission occurs with continuous digesters. However, batch digesters have the potential for releasing large quantities of sulphur dioxide, depending on how the digester is emptied. Digester and blow-pit emissions in the sulphite process vary depending on the type of system in operation. These areas have the potential for being a major source of sulphur dioxide emission. Pulp washers and multiple-effect evaporators also emit sulphur dioxide.

2.4   Mechanical Pulping

In mechanical pulping, pulp fibres are separated from the raw materials by physical energy such as grinding or shredding, although some mechanical processes use thermal and/or chemical energy to pretreat raw materials (Smook 1992;

Table 2.4 Volatile organic carbon emission from TMP mill before treatment. (Based on Nordic Council of Ministers 1993)

Process stage	
Sparkling washer	Total organic carbon: 6000 mg/m^3 (highest individual value: 9600 mg/m^3)
	Pinenes 1): 13,000 mg/m^3
Washing of woodchips	Total organic carbon: 300 mg/m^3
	Pinenes 1): 500 mg/m^3
Evacuation of air from other chests	Total organic carbon: 150 mg/m^3
	Pinenes 1): 50 mg/m^3

Biermann 1996). The main processes are stone groundwood pulping (SGW), pressure groundwood pulping (PGW), thermomechanical pulping (TMP) or chemithermomechanical pulping (CTMP). Emissions to the air are modest in mechanical pulping. Production emissions of purchased electricity can be high (Nordic Council of Ministers 1993). Atmospheric emissions from mechanical pulping are mainly linked to emissions of volatile organic compounds. Sources of volatile organic compounds emissions are evacuation of air from woodchips washing chests and other chests, and from sparkling washer where steam released in mechanical pulping processes contaminated with volatile wood components is condensed. The concentrations of volatile organic compounds depend on the quality and freshness of the raw material and the techniques applied. The emitted substances include acetic acids, formic acids, ethanol, pinenes and turpenes. Emissions of volatile organic compounds from a TMP mill before treatment is shown in Table 2.4

There are different alternatives for reducing volatile organic compounds emissions. Recovery of turpenes from those contaminated condensates that contain mainly turpenes or incineration of the exhaust gas in the on-site power plant or a separate furnace are available alternatives. In that case, about 1 kg volatile organic compounds/t of pulp is emitted from the process. Some volatile organic compounds may be released from wastewater treatment and unquantified emissions also occur from chip heaps.

In a CTMP mill, the atmospheric emissions originate mainly from chip impregnation and steam recovery (volatile organic compounds) and the bark boilers where wood residuals are burned (particulates, sulphur dioxide, NO$_x$) (European Commission 2001). As in other pulp and paper mills, mechanical pulping generates emissions to the air that are not process related but mainly related to energy generation by combustion of different types of fossil fuels or renewable wood residuals. The fossil fuels used are coal, bark, oil and natural gas. In a typical integrated paper mill that uses mechanical pulp high-pressure steam is generated in a power plant. The energy is partially transformed into electricity in a back pressure turbo generator and the rest is used in paper drying. The power plants burning solid fuels have electrostatic precipitators for the removal of particulates from the flue gases. The emission of sulphur dioxide is limited by using selected fuels. Depending on the local conditions there are paper mills using different amounts of energy from external supply.

References

Adams TN, Frederik WJ, Grace TM (1997) Kraft recovery boilers. TAPPI, Atlanta (USA 99)

Anderson K (1970) Formation of organic sulphur compounds during Kraft pulping. II. Influence of some cooking variables on the formation of organic sulphur compounds during kraft pulping of Pine. Svensk Paperstid 73(1):1

Andersson B, Lovblod R, Grennbelt P (1973) Diffuse emissions of odourous sulphur compounds from kraft pulp mills, 1 VLB145. Swedish Water and Air Pollution Research Laboratory, Gotenborg

Bajpai P (2008) Chemical recovery in pulp and paper making. PIRA International, U.K. 166 p

Biermann CJ (1996) Handbook of pulping and papermaking, 2nd edn. Academic, New York

Bordado JCM, Gomes JFP (1997) Pollutant atmospheric emissions from Portuguese Kraft pulp mills. Sci Total Environ 208(1–2):139–143

Bordado JCM, Gomes JFP (2003) Emission and odour control in kraft pulp mills. J Clean Prod 11:797–801

Dallons V (1979) Multimedia assessment of pollution potentials of non-sulphur chemical pulping technology. Environmental Protection Agency, Office of Research and Development, Industrial Environmental Research Laboratory, Cincinnati (EPA-600/2–79-026, January 1979)

Das TK, Jain AK (2004) Pollution prevention advances in pulp and paper processing. Environ Prog 20(2):87–92

EPA (2001a) Pulp and paper combustion sources National Emission Standards for Hazardous. U.S. Environmental Protection Agency, Office of Air and Radiation, Office of Air Quality Planning and Standards, Washington, DC

EPA (2001b) Pulping and bleaching system NESHAP for the pulp and paper Industry: a plain English description. U.S. Environmental Protection Agency. EPA-456/R-01–002. September 2001.http://www.epa.gov/ttn/atw/pulp/guidance.pdf. Accessed 12 Nov 2012

European Commission (2001) Integrated Pollution Prevention and Control (IPPC). Reference document on best available techniques in the pulp and paper industry. Institute for Prospective Technological Studies, Seville

Frederick WJ, Danko JP, Ayers RJ (1996) Control of TRS emissions from dissolving-tank vent stacks. TAPPI J 79(6):144

Gullichsen J (2000) Fibre line operations. In: Gullichsen J, Fogelholm C-J (eds) Chemical pulping—papermaking science and technology. Fapet Oy, Helsinki, p. A19 (Book 6 A)

Jarvensivu M, Lammi R, Kivivasara J (1997) Proceedings of the 1997 TAPPI Int. Environmental Conference, 645

Kringstad KP, McKean WT, Libert J, Kleppe PJ, Laishong C (1972) Odour reduction by in-digester oxidation of kraft black liquor with oxygen. TAPPI J 55(10):1528

Nordic Council of Ministers (1993) Study on Nordic pulp and paper industry and the environment. Nordic Council of Ministers, 1993

Pinkerton JE (1993) Emissions of SO_2 and NO_x from pulp and paper mills. J Air Waste Manag Assoc 43:1404–1407

Pinkerton J (1998) Trends in U.S. pulp and paper mill S and N emissions, 1980–1995. TAPPI J 181:114–122

Pinkerton J (2000a) Sulphur dioxide and nitrogen oxides emissions from pulp and paper mills in 2000. Special Report No. 02–06. National Council for Air and Stream Improvement, Inc., Research Triangle Park, NC, 2002

Pinkerton JE (2000b) Pulp and paper air pollution problems, Industrial environmental control. Pulp and paper industry. In: Springer AM (ed) 3rd edn. Atlanta, TAPPI, pp 501–535, 711 pp (Chap. 26)

Rydholm SA (1965) Pulping process. Wiley, New York, p 452

Smook GA (1992) Handbook for pulp & paper technologists, 2nd edn. Angus Wilde Publications, Vancouver

Someshwar AV (1989) Impact of burning oil as auxiliary fuel in kraft recovery furnaces upon SO_2 emissions. NCASI Technical Bulletin No. 578, December 1989

Someshwar AV, Pinkerton JE (1992) Wood processing industry. In: Buonicore AD, Davis WT (eds) Air pollution engineering manual. Van Nostrand Reinhold, New York

Springer AM, Courtney FE (1993) Air Pollution: a problem without boundaries. In: Springer AM (ed) Industrial environmental control pulp and paper industry, 2nd edn. TAPPI, Atlanta, pp 525–533

Tarpey T (1995) Odour reduction at [Daishowa- Marubeni International Ltd.'s] Peace River Pulp [Division Peace River Alberta]. International Environmental Conference Proceedings, 589

Tormund D, Teder A (1987) Elimination of malodourous organic sulphur compounds from the kraft pulping process with polythionate and sulfite. Nordic Pulp Paper Res J 2(3):97

US EPA (1973) Atmospheric emissions from the pulp and paper manufacturing industry. EPA-450/1-73-002. USEPA, Research Triangle Park

US EPA (1976) Environmental pollution control pulp and paper industry, Part 1, Air, U.S. EPA Technology Transfer Series, EPA-625/7-76-001, October 1976

US EPA (1986) Compilation of air pollutant emission factors, vol I. USEPA, Research Triangle Park

US EPA (1993a) Pulp, paper and paperboard industry background information for proposed air emission standards, manufacturing processes at kraft, sulfite, soda, and semi-chemical mills. EPA-453 R-93 – 050a. Office of Air Quality Planning and Standards, Research Triangle Park, NC27711

US EPA (1993b) Development document for proposed effluent limitations guidelines and standards for the pulp, paper and paperboard point source category. EPA-821-R-93-019. Office of Water, Mail Code 4303, Washington, DC

US EPA (2001) Air pollutants: a plain English description. EPA-456/R-01-003. September 2001. http://www.epa.gov/ttn/atw/pulp/Chaps.1-6pdf.zip. Accessed 18 Nov 2012

Wag KJ, Frederick WJ, Sricharoenchaikul V, Grace TM, Kymalainen MW (1995) Sulfate reduction and carbon removal during kraft char burning. International Chemical Recovery Conference: Preprints B, B35–50

Zhang Z, Luan G, Du P, Guo H (1999) More suitable process for dealing with the malodourous gases from sulfate cooking. Chin Pulp Paper Ind (4):16–18

Zhao H, Zhu J (2004) Operation experience of Kvaerner NCG System. Paper Paper Mak (1):21–23

Springer