

2.0 COMBUSTION PROCESSES IN THE KRAFT PULP INDUSTRY

This chapter describes the combustion processes and equipment associated with the chemical recovery cycle at kraft and soda pulp mills, as well as the HAP's emitted from these processes and equipment. The chemical recovery process includes four sources of HAP emissions that are the focus of this



document. These sources are (1) chemical recovery furnaces (including direct contact evaporator [DCE] recovery furnaces and nondirect contact evaporator [NDCE] recovery furnaces), (2) smelt dissolving tanks (SDT's), (3) black liquor oxidation (BLO) systems, and (4) lime kilns. Section 2.1 provides an overview of the kraft chemical recovery process. More detailed information on the combustion processes and equipment is included in Section 2.2. Section 2.3 presents existing Federal and State regulations affecting kraft pulp mills, process emission factors, and baseline HAP emissions. The references to this chapter are provided in Section 2.4.

2.1 OVERVIEW OF CHEMICAL RECOVERY PROCESSES

This section provides an overview of the chemical recovery cycle at kraft and soda pulp mills. References 1 and 2 listed in Section 2.4 provide more detailed descriptions of the chemical recovery cycle.^{1,2}

There are approximately 122 kraft pulp mills currently operating in the United States.³ There are only two soda mills currently operating in the United States.⁴ One soda mill is located in Pennsylvania and the other is located in Tennessee.⁴ Figure 2-1 shows the number of kraft and soda pulp mills located in each State. As shown in Figure 2-1, the majority (52 percent) of kraft pulp mills are located in the southeastern United

Figure 2-1. Distribution of U.S. kraft and soda pulp mills.

States. The kraft process is the dominant pulping process in the United States, accounting for approximately 85 percent of all domestic pulp production.⁵ The soda pulping process is similar to the kraft process, except that soda pulping is a nonsulfur process. One reason why the kraft process dominates the paper industry is because of the ability of the kraft chemical recovery process to recover approximately 95 percent of the pulping chemicals and at the same time produce energy in the form of steam. Other reasons for the dominance of the kraft process include its ability to handle a wide variety of wood species and the superior strength of its pulp.

The production of kraft and soda paper products from wood can be divided into three process areas: (1) pulping of wood chips, (2) chemical recovery, and (3) product forming (includes bleaching). The relationship of the chemical recovery cycle to the pulping and product forming processes is shown in Figure 2-2. Process flow diagrams of the chemical recovery area at kraft and soda pulp mills are shown in Figures 2-3 and 2-4, respectively. Kraft and soda chemical recovery processes are similar, except that the soda process does not require BLO systems, which are installed to reduce total reduced sulfur (TRS) emissions from DCE recovery furnaces. Both kraft and soda mills have chemical recovery furnaces, SDT's, and lime kilns. This document focuses on the four primary emission sources in the chemical recovery area. The emission sources covered in this document are the BLO system (kraft process only), the recovery furnace, the SDT, and the lime kiln. These emission sources are shaded in both process flow diagrams. Air emissions from these sources are expected to be similar for both kraft and soda processes, with the exception of TRS emissions. The soda process does not utilize sulfur-containing compounds; therefore, no TRS emissions are generated by soda mills.

Because of the similarities between the kraft and soda process and the predominant use of the kraft process, the information presented in the remainder of this document focuses on the kraft chemical recovery process.

Figure 2-2. Relationship of the chemical recovery cycle to the pulping and product forming processes.

Figure 2-3. Kraft process--chemical recovery area (DCE recovery furnace).

Figure 2-4. Soda process--chemical recovery area (DCE recovery furnace).

The purpose of the chemical recovery cycle is to recover cooking liquor chemicals from spent cooking liquor. The process involves concentrating black liquor, combusting organic compounds, reducing inorganic compounds, and reconstituting cooking liquor.

Cooking liquor, which is referred to as "white liquor," is an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) that is used in the pulping area of the mill. In the pulping process, white liquor is introduced with wood chips into digesters, where the wood chips are "cooked" under pressure. The contents of the digester are then discharged to a blow tank, where the softened chips are disintegrated into fibers or "pulp." The pulp and spent cooking liquor are subsequently separated in a series of brown stock washers. Spent cooking liquor, referred to as "weak black liquor," from the brown stock washers is routed to the chemical recovery area. Weak black liquor is a dilute solution (approximately 12 to 15 percent solids) of wood lignins, organic materials, oxidized inorganic compounds (sodium sulfate [Na_2SO_4], sodium carbonate [Na_2CO_3]), and white liquor (Na_2S and NaOH).

In the chemical recovery cycle, weak black liquor is first directed through a series of multiple-effect evaporators (MEE's) to increase the solids content to about 50 percent. The "strong" (or "heavy") black liquor from the MEE's is then either oxidized in the BLO system if it is further concentrated in a DCE or routed directly to a concentrator (NDCE). Oxidation of the black liquor prior to evaporation in a DCE reduces emissions of TRS compounds, which are stripped from the black liquor in the DCE when it contacts hot flue gases from the recovery furnace. The solids content of the black liquor following the final evaporator/concentrator typically averages 65 to 68 percent.

Concentrated black liquor is sprayed into the recovery furnace, where organic compounds are combusted, and the Na_2SO_4 is reduced to Na_2S . The black liquor burned in the recovery furnace has a high energy content (13,500 to 15,400 kilojoules per kilogram [kJ/kg] of dry solids [5,800 to 6,600 British thermal

units per pound {Btu/lb} of dry solids]), which is recovered as steam for process requirements, such as cooking wood chips, heating and evaporating black liquor, preheating combustion air, and drying the pulp or paper products. Particulate matter (PM) (primarily Na_2SO_4) exiting the furnace with the hot flue gases is collected in an electrostatic precipitator (ESP) and added to the black liquor to be fired in the recovery furnace. Additional makeup Na_2SO_4 , or "saltcake," may also be added to the black liquor prior to firing.

Molten inorganic salts, referred to as "smelt," collect in a char bed at the bottom of the furnace. Smelt is drawn off and dissolved in weak wash water in the SDT to form a solution of carbonate salts called "green liquor," which is primarily Na_2S and Na_2CO_3 . Green liquor also contains insoluble unburned carbon and inorganic impurities, called dregs, which are removed in a series of clarification tanks.

Decanted green liquor is transferred to the causticizing area, where the Na_2CO_3 is converted to NaOH by the addition of lime (calcium oxide [CaO]). The green liquor is first transferred to a slaker tank, where CaO from the lime kiln reacts with water to form calcium hydroxide ($\text{Ca}(\text{OH})_2$). From the slaker, liquor flows through a series of agitated tanks, referred to as causticizers, that allow the causticizing reaction to go to completion (i.e., $\text{Ca}(\text{OH})_2$ reacts with Na_2CO_3 to form NaOH and CaCO_3).

The causticizing product is then routed to the white liquor clarifier, which removes CaCO_3 precipitate, referred to as "lime mud." The lime mud, along with dregs from the green liquor clarifier, is washed in the mud washer to remove the last traces of sodium. The mud from the mud washer is then dried and calcined in a lime kiln to produce "reburned" lime, which is reintroduced to the slaker. The mud washer filtrate, known as weak wash, is used in the SDT to dissolve recovery furnace smelt. The white liquor (NaOH and Na_2S) from the clarifier is recycled to the digesters in the pulping area of the mill.

At about 7 percent of kraft mills, neutral sulfite semichemical (NSSC) pulping is also practiced.⁶ The NSSC process involves pulping wood chips in a solution of sodium sulfite and sodium bicarbonate, followed by mechanical defibrating. The NSSC and kraft processes often overlap in the chemical recovery loop, when the spent NSSC liquor, referred to as "pink liquor," is mixed with kraft black liquor and burned in the recovery furnace. In such cases, the NSSC chemicals replace most or all of the makeup chemicals. For Federal regulatory purposes, if the weight percentage of pink liquor solids exceeds 7 percent of the total mixture of solids fired and the sulfidity of the resultant green liquor exceeds 28 percent, the recovery furnace is classified as a "cross-recovery furnace."^{7,8} Because the pink liquor adds additional sulfur to the black liquor, TRS emissions from cross recovery furnaces tend to be higher than from straight kraft black liquor recovery furnaces.⁹

2.2 COMBUSTION PROCESSES AND EQUIPMENT

The following section describes the process and characterizes the equipment for: (1) recovery furnaces, (2) SDT's, (3) BLO systems, and (4) lime kilns.

The process descriptions presented in this section provide overviews of the various processes associated with the chemical recovery cycle. Much information is available on the kraft chemical recovery cycle and associated equipment; therefore, the process descriptions in this section do not cover every aspect of the chemical recovery cycle. Additional information about the chemical recovery cycle can be found in References 1, 2, and 10 through 13 listed in Section 2.4.^{1,2,10-13}

2.2.1 Recovery Furnaces

2.2.1.1 Process Description. The purpose of the kraft recovery furnace is to (1) recover inorganic pulping chemicals (e.g., Na_2S) and (2) produce steam. Inputs to the furnace include concentrated black liquor, combustion air, and auxiliary fuel (usually, auxiliary fuel is only used during shutdown or startup). Outputs include molten smelt (primarily Na_2S and Na_2CO_3), flue gases, and steam. The smelt exits from the bottom

of the furnace into a SDT tank, where the recovery of cooking chemicals continues. Particulate matter (primarily Na_2SO_4 and Na_2CO_3) entrained in the flue gases is also recovered using an ESP and subsequently added to the concentrated black liquor. Steam produced by the recovery furnace is used in other processes around the mill.

Prior to being fired in the recovery furnace, the black liquor is concentrated using an NDCE or DCE. Figures 2-5 and 2-6 show the equipment associated with NDCE and DCE recovery furnaces, respectively. The NDCE is an indirect, steam-heated black liquor concentrator. Black liquor typically enters the NDCE at a solids concentration of 50 percent and exits at a concentration of 68 percent or higher. The DCE uses the hot combustion gases exiting the furnace to increase the solids content of the black liquor from about 50 percent to 65 percent.

Direct contact evaporators may be of the cascade or cyclone design. Figures 2-7 and 2-8 present detailed diagrams of the cascade and cyclone designs, respectively. The cascade evaporator consists of a rotating assembly of tubes that are alternately submerged in black liquor and exposed to hot flue gases. A cyclone evaporator is a cylindrical vessel with a conical bottom. Black liquor is sprayed into the side of the evaporator, where it contacts the hot combustion gases that are introduced tangentially, creating a "cyclone" effect. The flue gases exit from the top of the evaporator, and the concentrated black liquor drains down to and exits from the bottom of the evaporator.²

To minimize the stripping of TRS compounds when the hot flue gases contact the black liquor in the DCE, most DCE's are preceded by BLO units, which stabilize the sulfur compounds in the black liquor. Black liquor that is concentrated in NDCE's does not contact the hot flue gases, and, therefore, does not require oxidation. Because the NDCE recovery furnace typically has lower TRS emissions than does the DCE recovery furnace, the NDCE recovery furnace is also referred to as the "low-odor"

Figure 2-5. Schematic of NDCE recovery furnace and associated equipment.

Figure 2-6. Schematic of DCE recovery furnace and associated equipment.

Figure 2-7. Cascade design evaporator.

Figure 2-8. Cyclone design evaporator.

design. Since the 1970's, most new recovery furnaces have been designed with NDCE's.

Regardless of how the black liquor is concentrated, the chemical reactions that take place inside an NDCE- or DCE-type furnace are the same. The concentrated black liquor is sprayed into the furnace through fixed or oscillating nozzles or "guns" mounted in the walls of the furnace. Depending upon the design and operation of the recovery furnace, the sprayed black liquor may hit the opposing wall, where it dries and burns before falling to the hearth, or may fall short of the opposing wall and dry and burn in suspension. Combustion air is generally supplied to the furnace at three levels, with two levels located below the black liquor nozzles and one above. Some furnaces may have only two combustion air levels (i.e., one above and one below the liquor nozzles).

The inorganic chemicals in the black liquor are recovered in three distinct zones inside the recovery furnace. Figure 2-9 shows where each zone is located in the furnace and the chemical reactions that take place in each zone. The area of the furnace extending from the black liquor spray to just above the molten smelt at the bottom of the furnace is referred to as the "drying zone." The purpose of the drying zone is to evaporate the water from the liquor droplets. The reducing zone is just below the drying zone and includes the char bed. The reduction of Na_2SO_4 to Na_2S takes place in the reducing zone. Volatile gases that are released in the drying and reducing zones of the furnace travel to the highly turbulent upper section of the furnace, referred to as the oxidizing zone, where the gases are combusted.² The heat generated from the combustion of these gases is then used to generate steam as the combustion gases are drawn through the heat exchanger section of the furnace (i.e., superheater, boiler bank, and economizer).

For NDCE recovery furnaces, the design economizer exit gas temperature ranges from 177° to 190°C (350° to 375°F).¹ For DCE recovery furnaces, the heat from the recovery furnace is used to evaporate the black liquor. Thus, the required economizer exit

Figure 2-9. Recovery furnace zones and air stages.

gas temperature for DCE recovery furnaces, 370° to 430°C (700° to 800°F), is much higher than that for NDCE recovery furnaces. Because a large portion of the combustion heat from DCE recovery furnaces is required for black liquor evaporation, less combustion heat is available to produce steam.

Flue gases exiting the economizer are routed either directly to a PM control device (i.e., for NDCE recovery furnaces) or to a DCE followed by a PM control device (i.e., for DCE recovery furnaces). The recovered PM (primarily Na₂SO₄ [saltcake] and Na₂CO₃) is subsequently added to the concentrated black liquor, and the cleaned flue gas exits through the stack. Approximately 95 percent of the Na₂SO₄ is recovered; additional makeup saltcake is added to the concentrated black liquor as needed.

The inorganic chemical in the black liquor, Na₂SO₄, is reduced to Na₂S, a cooking liquor chemical, in the reducing zone (lower section) of the furnace. The Na₂S and other inorganic chemicals, predominantly Na₂CO₃, drain as molten smelt from the furnace bottom to the SDT, where reprocessing into cooking liquor continues.

2.2.1.2 Equipment Characterization. An estimated 211 recovery furnaces operate at U.S. kraft pulp mills.³ Detailed information is available on about 85 percent of the estimated number of furnaces.¹⁴ Based on the available data, 61 percent of these recovery furnaces are NDCE recovery furnaces and 39 percent are DCE recovery furnaces.³ Eight percent of the recovery furnaces (76 percent of which are NDCE and 24 percent of which are DCE recovery furnaces) are located at kraft pulp mills that also practice NSSC pulping.⁶ The number of recovery furnaces at these mills that can be classified as cross-recovery furnaces is uncertain.

The nationwide distribution of DCE and NDCE recovery furnaces by age (i.e., original installation date) is provided in Figures 2-10a and 2-10b, respectively.³ As shown in Figures 2-10a and 2-10b, most recovery furnaces installed since the 1970's have been NDCE recovery furnaces. The first installation of a new NDCE recovery furnace took place in 1969.¹⁵

Figure 2-10a. DCE recovery furnace age distribution.

Figure 2-10b. NDCE recovery furnace age distribution.

Although Figure 2-10b shows that approximately 22 NDCE recovery furnaces currently in operation were installed in or before 1969, most, if not all of these furnaces were originally installed as DCE recovery furnaces and later converted to NDCE recovery furnaces. The most recent installation of a new DCE recovery furnace occurred in 1988; however, prior to 1988, the last installation of a new DCE recovery furnace was in 1979.³

The nationwide distribution of DCE and NDCE recovery furnaces by size (i.e., black liquor solids [BLS] feed rate) is provided in Figures 2-11a and 2-11b, respectively.³ The DCE recovery furnaces are not only typically older than NDCE recovery furnaces, but, as shown in Figures 2-11a and 2-11b, DCE recovery furnaces are also typically smaller. The majority of DCE recovery furnaces have a firing rate less than or equal to 900,000 kilograms of BLS per day (kg BLS/d) (2 million pounds of BLS/d [lb BLS/d]); whereas, the majority of NDCE recovery furnaces have firing rates greater than 900,000 kg BLS/d (2 million lb BLS/d).

The two furnace types also differ in the types of ESP's that are used to control particulate emissions from the furnace. For example, the ESP's that control PM emissions from DCE recovery furnaces tend to be wet-bottom ESP's (i.e., the PM catch falls directly into a pool of black liquor at the bottom of the ESP), whereas ESP's on NDCE recovery furnaces tend to be dry-bottom ESP's. Other differences between DCE and NDCE recovery furnaces include the following: (1) the inlet loading of PM to the ESP tends to be lower for DCE recovery furnaces than for NDCE recovery furnaces due to the recovery of some PM as the flue gases pass through the DCE; (2) emissions of TRS compounds tend to be higher from DCE recovery furnaces; and (3) NDCE recovery furnaces do not require black liquor oxidation, which eliminates one source of emissions.

Due to State and Federal regulations regarding PM emissions and the economic benefits of recycling PM captured from the recovery furnace flue gases, all kraft recovery furnaces are equipped with add-on PM control devices. Particulate matter

Figure 2-11a. DCE recovery furnace size distribution.

Figure 2-11b. NDCE recovery furnace size distribution.

emissions from approximately 95 percent of all kraft recovery furnaces are controlled with an ESP alone.³ The remaining furnaces are controlled with ESP's followed by wet scrubbers (4 percent) or with wet scrubbers alone (1 percent).³ Additional information on recovery furnace air pollution control devices (APCD's) and the effectiveness of these APCD's in controlling HAP emissions is provided in Chapter 3.

In general, recovery furnaces are not used to incinerate waste streams generated in other parts of the mill, with the exception of a few recovery furnaces (approximately 3 percent) that receive high-volume, low-concentration (HVLC) noncondensable gases (NCG's) from the pulping area of the mill.¹⁴ Because of the importance of the recovery furnace to the chemical recovery cycle and the potential for catastrophic explosion (due to water entering the furnace during operation), the industry's Black Liquor Recovery Boiler Advisory Committee (BLRBAC) recommends that the recovery furnace not be used for NCG incineration.¹

2.2.2 Smelt Dissolving Tanks

2.2.2.1 Process Description. Molten smelt is one of the main products from the combustion of black liquor. Smelt, which is predominantly Na_2S and Na_2CO_3 , is formed in the bottom of the furnace. Smelt, at approximately 1040° to 1150°C (1900° to 2100°F), filters through the char bed and is continuously discharged through water-cooled smelt spouts into the SDT. In the SDT, smelt is mixed with weak wash water from the recausticizing area to form green liquor, an aqueous solution of Na_2CO_3 and Na_2S in about a three to one ratio. The green liquor is subsequently transferred to the recausticizing area for reprocessing into cooking liquor (i.e., white liquor). A schematic of an SDT with a wet scrubber is provided in Figure 2-12.

The SDT is a large, covered vessel located below the recovery furnace. Green liquor is maintained in the tank at a level of about half the depth of the tank. As the smelt exits the water-cooled smelt spouts and falls several feet into the SDT, it is shattered by high-pressure steam or shatter sprays of

Figure 2-12. Smelt dissolving tank and wet scrubber.

recirculated green liquor. The steam or shatter sprays break the smelt flow into small droplets and cool the smelt before it falls into and reacts with the liquid in the SDT to form green liquor. Large volumes of steam are generated when the molten smelt and liquid mix. The vapor space above the liquid level provides an opportunity for water vapor and PM resulting from the quenching of smelt to settle out of suspension into the green liquor. An induced-draft fan constantly draws the vapor and entrained PM through a PM control device, generally a wet scrubber. Scrubber water is sprayed into the scrubber and allowed to drain directly into the SDT, where it reacts with smelt to form green liquor.

The SDT is constantly agitated to prevent formation of hot spots on the surface of the liquor and to keep solids from accumulating in the bottom of the tank. Surface liquor hot spots can contribute to the formation of explosive hydrogen gas from the dissociation of water reacting with the hot smelt.

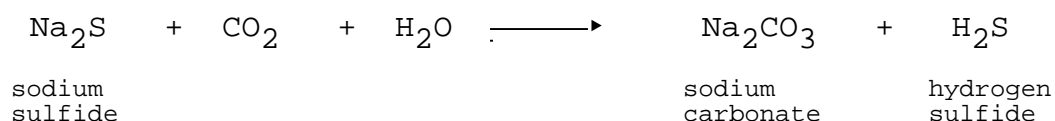
Green liquor formed in the SDT is sent to the green liquor clarifier in the causticizing area. Green liquor is converted to white liquor (i.e., NaOH and Na₂S) in the causticizing area.

2.2.2.2 Equipment Characterization. An estimated 227 SDT's operate at U.S. kraft pulp mills.³ Detailed information is available on approximately 83 percent of the estimated number of SDT's.⁶ Smelt dissolving tanks are basically large, covered tanks. Some recovery furnaces have two SDT's, which explains why the estimated number of SDT's is higher than the estimated number of recovery furnaces. When there are two SDT's under one furnace, the flue gases from these SDT's may be combined or treated separately.

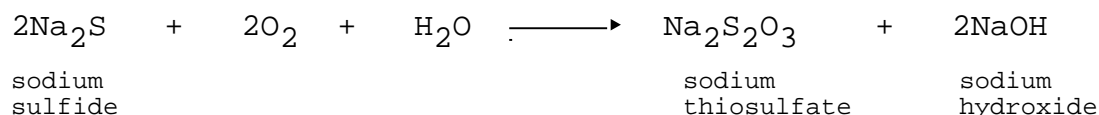
Due to State and Federal regulations regarding PM emissions, all but two kraft SDT's are equipped with add-on PM control devices. Particulate matter emissions from approximately 87 percent of kraft SDT's are controlled with wet scrubbers.¹⁴ Particulate matter emissions from most of the remaining SDT's are controlled with mist eliminators alone.¹⁴ Additional information on SDT APCD's and the effectiveness of these APCD's in controlling HAP emissions is provided in Chapter 3.

2.2.3 Black Liquor Oxidation Systems

2.2.3.1 Process Description. The BLO system reduces malodorous TRS emissions from DCE recovery furnaces at kraft pulp mills. Total reduced sulfur compounds (primarily hydrogen sulfide [H₂S]) are stripped from black liquor when hot flue gases from the recovery furnace contact the black liquor in the DCE. Hydrogen sulfide is stripped by the reaction between residual Na₂S in the black liquor and carbon dioxide (CO₂) and water (H₂O) in the recovery furnace flue gas, as follows:



The BLO system minimizes the stripping of TRS compounds in the DCE by stabilizing the sulfur compounds in the black liquor prior to evaporation in the DCE. The main reaction that takes place in the BLO system is the oxidation of Na₂S to nonvolatile sodium thiosulfate (Na₂S₂O₃), as follows:



The oxidation efficiency of the BLO process is measured by the percent conversion of Na₂S to Na₂S₂O₃ in the black liquor on a gram per liter (g/L) (pound per gallon [lb/gal]) basis. Oxidation efficiencies greater than 99 percent are common. High oxidation efficiencies require good mixing and the avoidance of excessive oxygen (O₂) consumption to limit side reactions. Sulfidity levels of the black liquor entering the DCE are targeted to less than 0.2 g/L (0.002 lb/gal) in order to meet TRS emission limits for DCE recovery furnaces.¹ Oxidizing black liquor results in a slight increase (2 to 3 percent) in the solids content of the black liquor and reduces its heating value by 2 to 5 percent.¹⁶

The BLO system is typically located after the MEE, a process referred to as "strong" black liquor oxidation. A small number of mills oxidize black liquor prior to evaporation in the MEE, which is referred to as "weak" black liquor oxidation. Other options are to oxidize both weak and strong black liquor or to oxidize the black liquor between effects of the MEE. To avoid excessive foaming caused by tall oil components in weak black liquor, mills in the south that pulp pine oxidize strong black liquor. With strong black liquor, the soaps and tall oil are removed during the soap-skimming process that follows black liquor evaporation in the MEE. With weak BLO systems, the effects of partial reversing of the oxidation reaction (i.e., oxidized sulfur compounds reducing to H₂S) that occurs in the MEE can be minimized by adding a second oxidation step, such as oxygen polishing of strong black liquor.

Black liquor can be oxidized using either air or pure (molecular) O₂. Because of economic considerations, the majority of BLO systems use air as the oxidant. Air BLO systems have higher capital costs than oxygen systems, but their operating costs are usually much lower.

Air-sparging units are the predominant type of BLO equipment used at kraft pulp mills. Figure 2-13 shows a schematic of an air-sparging BLO system. Air-sparging units operate by bubbling air, which is sometimes preheated, through the black liquor using multiple diffuser nozzles. Air systems require residence times of several hours or more to obtain high oxidation efficiencies. Because of this relatively long residence time, large oxidation tanks--on the order of 9 meters (m) (30 feet [ft]) in diameter and 12 m [40 ft] high) must be used. Air-sparging units have one to three tanks (or stages) that operate in series. Air-sparging units are equipped with mechanical foam breakers for foam control; chemical defoamers (e.g., diesel oil, turpentine, and kerosene) may also be used.^{1,12} Each oxidation tank is vented. Gases exiting the BLO system flow through cyclone separators to have entrained water droplets removed prior to being vented to

Figure 2-13. Two-stage air-sparging black liquor oxidation system.

the atmosphere. Add-on APCD's typically are not used with air oxidation units.

Oxygen BLO systems require only 30 seconds (sec) to 5 minutes (min) residence time, which enables the use of in-line reactors. Since all the gas (i.e., pure O₂) added to the system is consumed in the oxidation reaction, a system vent is not needed.¹⁶ The oxygen consumption for weak black liquor oxygen systems is 25 to 65 kilograms per megagram (kg/Mg) of pulp (50 to 130 pounds per ton [lb/ton] of pulp); strong black liquor oxygen systems use 35 to 75 kg O₂/Mg pulp (70 to 150 lb O₂/ton pulp.)¹⁷

Oxygen polishing is sometimes used as a supplement to air oxidation systems to address (1) stricter TRS standards, (2) an overloaded BLO system resulting from production increases, or (3) peaks in TRS emissions resulting from process upsets or temporary production increases. In-line O₂ polishing systems are used to oxidize strong liquor and may follow either a weak liquor air system or a strong liquor air system. Polishing of strong black liquor requires approximately 2.5 to 13 kg O₂/Mg pulp (5 to 25 lb O₂/ton pulp) to achieve the desired incremental increases in oxidation efficiency.¹⁷

2.2.3.2 Equipment Characterization. Of the 47 U.S. kraft pulp mills that operate DCE recovery furnaces, only 1 (with 1 DCE recovery furnace) is known to operate without a BLO system. Therefore, the nationwide number of BLO systems is estimated to be 46.³ Detailed information is available on approximately 91 percent of the estimated U.S. population.^{14,18} The type of equipment operated and the type of liquor oxidized for the BLO systems is summarized in Table 2-1.³ Oxidation of strong black liquor using air-sparging units is the predominant method of black liquor oxidation and accounts for an estimated 89 percent of the U.S. population.³ Seven percent of the mills operating air-sparging units also have added O₂ polishing systems. Of the air-sparging BLO systems, 50 percent are two-stage systems, 31 percent are single-stage systems, and 18 percent have three oxidation tanks.¹⁴

TABLE 2-1. BLACK LIQUOR OXIDATION SYSTEMS: EQUIPMENT TYPES³

Equipment type	Liquor type	Estimated No. in U.S.	Percent
Air sparging	Strong	38	83
Air sparging with O ₂ polishing	Strong	3	7
Air, sieve tray tower	Weak	1	2
Molecular O ₂	Strong	2	4
Molecular O ₂	Weak	1	2
Molecular O ₂	Weak and strong	1	2
Total	--	46	100

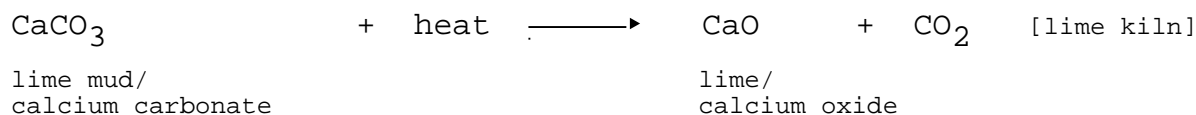
Approximately 8.5 percent of BLO systems are molecular O₂ systems.³ Strong black liquor is oxidized with O₂ after the second effect of the MEE (26 percent solids) at two of the four mills; weak black liquor (i.e., prior to the MEE) is oxidized at another mill; and both weak and strong liquor are oxidized with O₂ at the fourth mill.^{3,14} One mill with a BLO system located after the second effect of the MEE reported an oxygen usage rate of 32 Mg/d (35 ton/d) (13 kg/Mg pulp [25 lb/ton pulp]).¹⁴

Emissions from most air-based BLO systems (95 percent) are uncontrolled.³ Based on available information, TRS emissions from 5 percent of air-based BLO systems are currently controlled by using a condenser or mist eliminator to remove the water vapor and then venting the gas stream to a power boiler for incineration.¹⁴ Molecular O₂ systems do not require system vents and, thus, have no emissions directly associated with the BLO unit.¹³

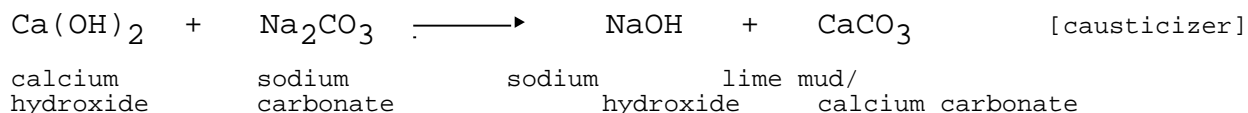
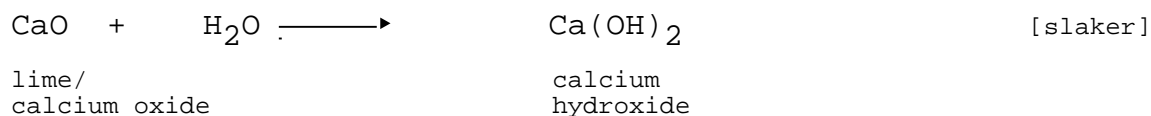
2.2.4 Lime Kilns

2.2.4.1 Process Description. The lime kiln is part of the causticizing process, in which green liquor from the SDT is converted to white liquor. The function of the lime kiln is to

convert lime mud (calcium carbonate [CaCO₃]) to reburned lime (calcium oxide [CaO]), a process known as calcining:



Lime mud that is burned in the lime kiln is a final product of the following causticizing reactions:



Lime that is produced in the kiln is used in the causticizing reaction that takes place in the green liquor slaker and causticizers. The lime kiln typically produces about 95 percent of the lime needed for the causticizing reaction. Either make-up lime or limestone is purchased to account for losses.

Prior to calcining, lime mud from the causticizing tanks is washed and dewatered. Lime mud washers reduce the sodium and sulfide content of the lime mud, which lowers TRS emissions from the lime kiln. The lime mud is typically dewatered to about 70 percent solids using a rotary vacuum precoat filter. The precoat filter also helps reduce TRS emissions by oxidizing any remaining sodium sulfide to sodium thiosulfate using air that is pulled through the filter.

Rotary lime kilns, as shown in Figure 2-14, are typically used at kraft pulp mills. In a rotary kiln, lime mud from the precoat filter is introduced at the feed end (cold end) and flows downward towards the discharge end (hot end). The chemical composition of the lime mud is presented in Table 2-2. Natural gas or fuel oil are the fuels typically used to fire the kiln.

Figure 2-14. Schematic of a lime kiln used at kraft pulp mills.

TABLE 2-2. CHEMICAL COMPOSITION OF LIME MUD FEED²⁰

Component	Composition (%)
Calcium carbonate	>95
Alumina	<0.5
Iron oxide	<0.5
Calcium oxide	<0.5
Sodium oxide	<0.2
Silica	<0.2
Sodium sulfide	<0.01

Primary combustion air is introduced through a concentric tube around the fuel pipe, and preheated secondary combustion air is introduced through the bottom of the firing hood.

The majority of lime kilns at kraft pulp mills also burn NCG's from various process vents, such as digester and evaporator vents. The NCG streams may be introduced into the kiln through a dedicated nozzle or combined and fed with either primary or secondary air. The components of the NCG stream include TRS compounds, turpentine, methanol, acetone, alpha-pinene, water vapor, nitrogen, and oxygen.^{1,19} To avoid excessive sulfur dioxide (SO₂) formation in the lime kiln, the NCG gas stream may be scrubbed prior to incineration to remove TRS compounds. Packed columns with white liquor as the scrubbing fluid are commonly used. The TRS removal efficiency is typically about 70 percent.¹

Rotary kilns have three internal zones: (1) the drying zone, (2) the heating zone, and (3) the calcining zone. In the drying zone, water is evaporated from the lime mud as it passes through metal chains that are suspended from the kiln shell in a curtain or garland arrangement. The lime mud is dried to about 95 percent or greater solids as it passes through the chains that are heated by the hot flue gases that flow countercurrent to the lime mud. In addition to providing additional heat transfer area for drying the lime mud, the chains also help reduce the amount

of lime dust exiting with flue gases. In the heating zone, other heat transfer devices, such as tumblers and lifters, are used to heat the dried mud uniformly in preparation for calcining. The calcining reaction, which takes place in the calcining zone, requires a minimum temperature of 815°C (1500°F); temperatures greater than about 1150°C (2100°F) can cause overburning, which leads to a less-reactive lime product.¹ Ideally, calcination produces lime pellets that are about 2 centimeters (cm) (0.75 inches [in.]) in diameter; however, if the lime mud is improperly dried and heated, large lime balls may be produced.¹ The hot lime product is cooled by incoming secondary air as it passes under the burner towards the discharge end of the kiln. Newer kilns use integral tube coolers to preheat secondary combustion air while cooling the discharged lime pellets. In this heat exchange process, the air is heated to about 315°C (600°F) and the lime is cooled to about 190°C (375°F). The reburned lime product from the integral tube coolers, or from the kiln discharge hoppers in the absence of coolers, is transported to the lime storage bin and subsequently introduced into the green liquor slaker.

Combustion gases exit the lime mud feed end of the kiln at temperatures of approximately 150° to 200°C (300° to 400°F). The exhaust gases consist of combustion products, CO₂ released during calcination, water vapor evaporated from the mud, and entrained lime dust. Particulate matter in the exhaust gas is mainly sodium salts, CaCO₃, and CaO. Add-on PM control devices are required to meet Federal and State PM standards. Venturi scrubbers are the most commonly used control device, and water is typically used as the scrubbing fluid. The exhaust stream may be scrubbed with a caustic solution with the added benefit of lowering TRS and SO₂ emissions. However, Federal and State TRS standards can be met through good lime mud washing practices, which reduces the sulfide content of the lime mud feed. If a wet scrubber is used, a cyclone separator may be installed upstream. The dust collected by the separator is returned directly to the lime kiln. In recent years, the use of ESP's has been more

prevalent. As with the cyclone separator, the PM catch from the ESP is returned directly to the lime kiln.

2.2.4.2 Equipment Characterization. An estimated 192 lime kilns operate at U.S. kraft pulp mills.³ Detailed information is available on about 85 percent of the estimated number of lime kilns.¹⁴ Rotary kilns are the most commonly used type of lime kiln at kraft pulp mills, accounting for about 98 percent of the kilns.^{6,21} Fluidized-bed calciners are also used by the kraft pulp industry. Industry representatives estimated the number of fluidized-bed calciners at two to five, accounting for the remaining 2 percent of lime kilns at kraft pulp mills.^{6,21} Based on available data, the oldest operating lime kiln was installed in 1940.¹⁴ New lime kilns were installed at a rate of approximately three kilns per year from 1981 to 1991.¹⁴

The predominant fuel used by the industry is natural gas, accounting for about 68 percent of lime kilns.¹⁴ Fuel oil is the primary fuel for about 29 percent of kilns.¹⁴ Petroleum coke is fired in about 3 percent of the kilns as the primary fuel.

Due to State and Federal regulations regarding PM emissions, all lime kilns are equipped with add-on PM control devices. Particulate matter emissions from the majority (90 percent) of lime kilns at kraft pulp mills are controlled with wet scrubbers. Two percent of these scrubbers are operated in series with a second scrubber. Venturi scrubbers are the most commonly used type of wet scrubber.¹⁴ Water is the typical scrubbing fluid, but caustic and weak wash are also used.¹⁴ The scrubbing fluid is recirculated, and the scrubber blowdown is recycled to the lime mud washer. Particulate matter emissions from the remaining 10 percent of lime kilns are controlled by single-chamber ESP's (9 percent) or the combination of an ESP and scrubber (1 percent).¹⁴ Installing ESP's to control PM from lime kilns has been more widespread in recent years; about half of the APCD installations since 1990 have been ESP's.

An estimated 66 percent of lime kilns are either primary or backup incineration devices for NCG streams.¹⁴ Of the lime kilns that incinerate NCG's, 57 percent incinerate low-volume, high-

concentration (LVHC) NCG streams; 28 percent incinerate HVLC NCG streams; and 24 percent incinerate both LVHC and HVLC NCG streams. Approximately 33 percent of the lime kilns in which NCG's are incinerated use an NCG scrubber prior to incineration.¹⁴ The majority of these NCG scrubbers use white liquor as the scrubbing fluid; a small percentage use water.

2.3 BASELINE EMISSIONS

2.3.1 Federal and State Regulations Affecting Kraft Pulp Mill Combustion Sources

Federal regulations that affect the pulp and paper industry include new source performance standards (NSPS) for kraft pulp mills. The NSPS does not include soda mills. The NSPS specifies PM and TRS emission limits for various pulp mill equipment that are constructed, modified, or reconstructed after September 24, 1976.^{7,8} Recovery furnaces, SDT's, and lime kilns are regulated under the kraft pulp mill NSPS.

The percentage of recovery furnaces, SDT's, and lime kilns that are subject to the NSPS were estimated using installation dates. These estimates, therefore, do not include those recovery furnaces, SDT's, and lime kilns that are subject to the NSPS through the modification/reconstruction provisions. Approximately 4 percent (i.e., 3 of 83) of the DCE recovery furnaces and 39 percent (50 of 128) of the NDCE recovery furnaces are subject to the NSPS.³ Based on recovery furnace installation dates, approximately 29 percent of the SDT's are subject to the NSPS.³ Approximately 28 percent of the lime kilns are subject to the NSPS.¹⁴ Nine new BLO systems have been installed since the 1976 NSPS proposal for kraft pulp mills; eight of these new BLO systems are still in operation, making up 17 percent of the existing population of operating BLO systems.¹⁸

Table 2-3 lists the NSPS PM and TRS emission limits. The EPA TRS emission limit guidelines for sources not subject to the NSPS are also listed in Table 2-3. The TRS guidelines are the same as the NSPS emission limits for NDCE and cross-recovery furnaces. The NSPS emission limit is 5 parts per million dry volume (ppmdv) at 8 percent O₂. For DCE recovery furnaces, the

TABLE 2-3. NSPS AND EMISSION GUIDELINES FOR KRAFT PULP MILL COMBUSTION SOURCES^a

Source	Particulate matter--NSPS	Total reduced sulfur	
		NSPS	Guidelines ^b
NDCE recovery furnace	0.10 g/dscm (0.044 gr/dscf) @ 8% O ₂	5 ppm _{dv} @ 8% O ₂	5 ppm _{dv} @ 8% O ₂
DCE recovery furnace	0.10 g/dscm (0.044 gr/dscf) @ 8% O ₂	5 ppm _{dv} @ 8% O ₂	20 ppm _{dv} @ 8% O ₂
Cross recovery furnace ^c	0.10 g/dscm (0.044 gr/dscf) @ 8% O ₂	25 ppm _{dv} @ 8% O ₂	25 ppm _{dv} @ 8% O ₂
Smelt dissolving tank ^d	0.10 kg/Mg (0.20 lb/ton) BLS	0.016 kg/Mg (0.033 lb/ton) BLS	---
Lime kiln (gas-fired)	0.15 g/dscm (0.067 gr/dscf) @ 10% O ₂	8 ppm _{dv} @ 10% O ₂	20 ppm _{dv} @ 10% O ₂
Lime kiln (liquid-fired)	0.30 g/dscm (0.13 gr/dscf) @ 10% O ₂	8 ppm _{dv} @ 10% O ₂	20 ppm _{dv} @ 10% O ₂
Black liquor oxidation ^e	--	No control	No control

2-35

^ag/dscm = grams per dry standard cubic meter

gr/dscf = grains per dry standard cubic foot

kg/Mg BLS = kilograms per megagram of black liquor solids

lb/ton BLS = pounds per ton of black liquor solids

ppm_{dv} = parts per million dry volume

^bEPA guidelines for TRS emissions from kraft pulp mills not subject to the NSPS; ppm_{dv} = ppm dry on volume basis.

^cIf the weight percentage of pink liquor solids exceeds 7 percent of the total mixture of solids fired and the sulfidity of the resultant green liquor exceeds 28 percent, the recovery furnace is classified as a "cross-recovery furnace."^{7,8}

^dBLS = black liquor solids.

^eEPA originally promulgated a TRS emission limit for BLO units of 5 ppm; this requirement was rescinded during the NSPS review.

TRS guidelines are 20 ppmdv at 8 percent O₂, which are higher than the NSPS limit. Similarly, the TRS guidelines for lime kilns (20 ppmdv at 10 percent O₂) are higher than the NSPS limit (8 ppmdv at 10 percent O₂). The TRS compounds are hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. None of these TRS compounds are currently listed in the Clean Air Act for regulation under Section 112. However, PM emitted from kraft pulp mill sources does contain small amounts of HAP compounds (e.g., HAP metals).

State regulations for PM and TRS emissions for new, modified, and reconstructed recovery furnaces, lime kilns, and SDT's are the same as Federal regulations, with a few exceptions.²² The State of Georgia has promulgated process-weighted standards for PM, which, for some Georgia mills, are slightly more stringent than the NSPS PM limits. Also, the State of Alabama requires new sources to use the "highest and best practicable controls for PM."²² In addition, several States regulate toxic air emissions from pulp mills. These regulations, however, tend to limit the concentration of air toxics at the pulp mill fence line, and thus do not directly regulate emissions from specific equipment in the chemical recovery area of the mill. For existing recovery furnaces that are not subject to the NSPS, most States have emission standards equivalent to or more stringent than the EPA TRS emission limit guidelines.^{22,23} For existing lime kilns that are not subject to the NSPS, approximately half of the States with kraft mills have emission standards equivalent to or more stringent than the EPA TRS emission limit guidelines.^{22,23}

2.3.2 Baseline Emission Estimates

Section 2.3.2.1 presents the baseline gaseous HAP emission estimates from combustion sources at kraft and soda pulp and paper mills. Baseline gaseous HAP emissions were developed for DCE recovery furnaces, NDCE recovery furnaces, and BLO systems. Baseline gaseous HAP emissions were not developed for lime kilns and SDT's because the gaseous HAP emissions from these units result from the use of contaminated condensates in the makeup

waters. The regulation of contaminated condensates is part of the noncombustion source category for kraft and soda pulp and paper mills. Section 2.3.2.2 presents baseline PM and TRS emissions from combustion sources at kraft and soda pulp and paper mills.

2.3.2.1 Baseline Gaseous HAP Emissions. Table 2-4 presents gaseous HAP process emission factors for the two types of recovery furnaces (DCE and NDCE) used in the kraft chemical recovery loop. The process emission factors were calculated based on available emission test data and process emission rates for each of the recovery furnaces.²⁴ In the case of DCE recovery furnace systems, emission points include the recovery furnace/DCE stack and the BLO vent. The only emission point associated with NDCE recovery furnaces is the recovery furnace stack. As shown in Table 2-4, the gaseous HAP compounds emitted in the largest quantities from DCE and NDCE recovery furnaces are hydrochloric acid (HCl) and methanol. The following sections discuss the potential mechanisms by which HCl and gaseous organic HAP's such as methanol are emitted, as well as the nationwide emissions of these pollutants.

2.3.2.1.1 HCl emissions. Typically, HCl emissions from combustion processes are generated from oxidation reactions involving chlorinated organic compounds in the fuel, and all of the organic chlorine in the fuel is presumed to be emitted as HCl. However, chlorine in black liquor is expected to be in the form of inorganic chlorine. Consequently, only a small fraction (0 to 10 percent) of the black liquor chlorine is believed to be emitted from the recovery furnace as HCl.²⁵ A possible mechanism for HCl formation in the recovery furnace is gas phase reactions of volatilized alkali chlorides with SO₂ in the presence of water vapor and oxygen.^{25,26} The proposed reactions are as follows:^{25,26}

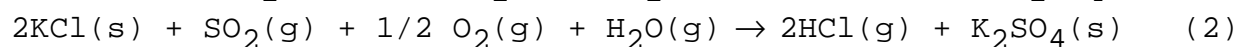
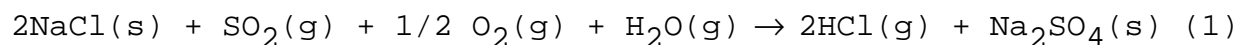


TABLE 2-4. HAP EMISSION FACTORS

HAP	Emission factors, mass/mass BLS fired				
	DCE recovery furnace systems		NDCE recovery furnaces		
	Air-sparging BLO system ^a	DCE recovery furnace	Dry ESP system ^b	Wet ESP system ^c	Average ^d
Acetaldehyde	1.48×10^{-5}	2.99×10^{-5}	1.52×10^{-5}	7.50×10^{-6}	1.03×10^{-5}
Benzene	1.21×10^{-6}	1.45×10^{-5}	1.73×10^{-6}	9.73×10^{-6}	7.97×10^{-6}
Formaldehyde	2.89×10^{-7}	2.82×10^{-6}	1.93×10^{-6}	2.98×10^{-6}	9.20×10^{-6}
Methyl ethyl ketone	4.24×10^{-6}	8.53×10^{-6}	1.80×10^{-6}	7.46×10^{-6}	6.59×10^{-6}
Methyl isobutyl ketone	1.77×10^{-6}	1.21×10^{-5}	2.27×10^{-6}	9.23×10^{-6}	8.17×10^{-6}
Methanol	1.73×10^{-4}	1.70×10^{-4}	4.93×10^{-6}	5.04×10^{-5}	3.71×10^{-5}
Phenol	1.93×10^{-6}	3.95×10^{-5}	2.05×10^{-6}	1.50×10^{-5}	1.62×10^{-5}
Toluene	1.44×10^{-6}	9.73×10^{-6}	2.03×10^{-6}	8.37×10^{-6}	7.41×10^{-6}
Xylenes	4.28×10^{-6}	2.47×10^{-5}	4.76×10^{-6}	1.92×10^{-5}	1.70×10^{-5}
Hydrochloric acid	N/A	1.20×10^{-4}	1.20×10^{-4}	1.20×10^{-4}	1.20×10^{-4}
Total HAP	2.03×10^{-4}	4.32×10^{-4}	1.57×10^{-4}	2.50×10^{-4}	2.40×10^{-4}

^aFor the BLO systems, the emission factors are based on equivalent BLS firing rates.

^bDry ESP systems include a dry-bottom ESP and a dry PM return system.

^cWet ESP systems include wet-bottom ESP's and those dry-bottom ESP's that use black liquor or HAP-contaminated water in the PM return system.

^dThe average represents the average emission factor calculated based on all available data for NDCE recovery furnaces.

These reactions are believed to occur at temperatures below about 900°C (1650°F) in the furnace post-combustion zone and in higher temperature areas in the ductwork downstream from the furnace.^{25,26} Assuming the above reactions are the correct mechanism for HCl formation, HCl emissions will be higher for well-designed and operated combustion systems. Combustion system parameters that could potentially affect the amount of HCl formed include higher combustion zone temperatures leading to greater emissions of volatile sodium chloride (NaCl) and potassium chloride (KCl), furnace SO₂ generation rates, and good mixing of combustion gases with excess air in the post-combustion zone.

A review of the available emissions data indicates that HCl emissions from recovery furnaces are highly variable. A recent study of kraft recovery furnace HCl emissions conducted by the National Council of the Paper Industry and Air and Steam Improvement, Inc. (NCASI) examined the relationships between several recovery furnace operating parameters and HCl emissions.²⁷ Some earlier studies had suggested that there may be strong correlations between stack SO₂ emissions and HCl emissions and between stack O₂ concentration and HCl emissions.^{25,26} The NCASI study, which was based on tests of 14 recovery furnaces conducted specifically for this study, examined the relationship between HCl emissions and each of the following parameters: stack SO₂ concentration, as-fired black liquor chloride content, stack O₂ levels, chloride content of precipitated ash, and furnace load or liquor firing rate.²⁷ Based only on the tests conducted in this study, NCASI found a strong correlation using a Langmuir adsorption-type relationship between HCl emissions and SO₂ emissions for NDCE recovery furnaces and found no clear correlation between these parameters for DCE recovery furnaces.²⁷ The study found no clear correlations between HCl emissions and other recovery furnace operating parameters.²⁷

As shown in Table 2-4, the HCl emission factor presented for both NDCE and DCE recovery furnace systems is the same. Based on a statistical analysis of the available HCl emissions data, it

was concluded that the NDCE and DCE recovery furnace HCl emission factors should be averaged together. The range of HCl emission factors for NDCE recovery furnaces extends above and below the range of factors for DCE recovery furnaces. Both the 90 and 95 percent confidence intervals of the difference between the DCE and NDCE recovery furnace means include zero. Stated another way, the hypothesis that the means are equal cannot be rejected at the 0.1 and 0.05 levels of significance.²⁸

2.3.2.1.2 Gaseous organic HAP emissions. Methanol and other gaseous organic HAP's are emitted from process units throughout the chemical recovery area of the pulp mill. The primary mechanism for gaseous organic HAP emissions from recovery furnace stacks is the stripping of gaseous organic HAP's from black liquor, which occurs when hot flue gases directly contact the black liquor. Gaseous organic HAP's are also emitted from the BLO vent as a result of stripping of these HAP's from the black liquor as the oxidizing air is forced up through the liquor.

The emission potential for DCE recovery furnace systems (which include the DCE recovery furnace and the BLO unit) is significantly higher than for NDCE recovery furnaces because of the increased opportunity for stripping of HAP compounds from black liquor in process equipment. In the DCE recovery furnace system, opportunities for stripping of HAP's exist in (1) air-based BLO systems, (2) DCE's, and (3) ESP systems (i.e., the ESP and the PM return system associated with the ESP). However, with NDCE recovery furnaces, the ESP system is the only process equipment where stripping of HAP's may occur.

Methanol emission test data are available for DCE recovery furnaces equipped with air-sparging BLO systems. These data show that the total amount of methanol emitted from the BLO vents and DCE recovery furnace stack (which includes any methanol stripped in the DCE and ESP) at a given mill will vary, as will the quantity of methanol emitted from each source. Tests conducted at one mill showed that methanol emissions from the two sources were related (i.e., if methanol emissions from the BLO vents were

high, then methanol emissions from the DCE recovery furnace stack were low).²⁹

No emission data are available from DCE recovery furnaces with molecular oxygen BLO systems for comparison with DCE recovery furnaces with air-based BLO systems. Therefore, the effect of molecular oxygen BLO systems on total emissions from the DCE recovery furnace system is uncertain. Unlike air-based systems, molecular oxygen systems use pure oxygen, and thus, no diluents are introduced that could strip organic compounds from the black liquor; consequently, organic compounds not released from the black liquor during the oxidation process could be subsequently stripped, in theory, from the oxidized black liquor when the black liquor enters the ESP or direct contact evaporator.

Most DCE recovery furnaces and some older NDCE recovery furnaces are equipped with wet ESP systems. Either black liquor or HAP-contaminated process water may be present in the bottom of these ESP's and in the system used to transport the collected PM to the saltcake mix tank. Also, for wet ESP systems, the PM may be collected as a dry product in the bottom of the ESP (i.e., a dry-bottom ESP) but black liquor or HAP-contaminated water is used in the PM return system. Because there is contact between the hot recovery furnace flue gases and the black liquor or HAP-contaminated process water in wet ESP systems, gaseous organic HAP's are stripped from the liquor and emitted from the recovery furnace stack. Most newer NDCE recovery furnaces (i.e., those constructed after 1989) emit lesser quantities of methanol and other gaseous organic HAP's because they tend to be equipped with dry ESP systems (i.e., dry-bottom ESP's and dry PM return systems).³⁰

Data are not available to determine the effects of converting a wet ESP system to a dry ESP system on overall gaseous HAP emissions for a DCE recovery furnace system. Gaseous organic HAP's that would have been stripped from the black liquor in the wet ESP system potentially could be stripped from the black liquor when it enters the DCE. Also, based on emission

data for NDCE recovery furnaces with wet ESP systems, the ESP is a less significant source of gaseous organic HAP emissions than the BLO or DCE. Data are available for NDCE recovery furnaces with both wet ESP systems and dry ESP systems such that the impacts that different ESP systems have on gaseous organic HAP emissions from NDCE recovery furnaces can be determined. These impacts can be more readily determined since the ESP represents the only opportunity where stripping can occur for NDCE recovery furnaces.

2.3.2.1.3 Nationwide gaseous HAP emissions. Table 2-5 presents the nationwide baseline gaseous HAP emissions from recovery furnaces. The nationwide baseline total gaseous HAP emissions from the estimated 128 NDCE recovery furnaces are estimated to be 13,700 megagrams per year (Mg/yr) (15,100 tons per year [ton/yr]). The nationwide baseline total gaseous HAP emissions from the estimated 83 DCE recovery furnace systems (which includes BLO systems) are estimated to be 15,700 Mg/yr (17,300 ton/yr). The baseline emissions shown in Table 2-5 were calculated assuming no control of gaseous HAP's (with the exception of the two BLO systems with emissions controlled via incineration) because gaseous HAP emissions from recovery furnaces are highly variable and largely uncontrolled. The baseline emissions were calculated by multiplying the gaseous HAP emission factors by the process emission rate in kg BLS/hr (lb BLS/hr) for each mill for which data were available and then extrapolating based on the available data to account for those mills where data were unavailable. The baseline emissions were also calculated based on the assumption that each emission source operates 24 hours per day (hr/d) for 351 days per year (d/yr).²⁴

2.3.2.2 Baseline PM and TRS Emissions. Table 2-6 presents nationwide total PM, PM HAP, and TRS baseline emissions from each combustion source. The HAP portion of total PM consists of HAP metals and accounts for less than 1 percent of the total PM emitted on average; therefore, only the total estimated quantity of HAP metals are presented in Table 2-6, instead of presenting emission estimates for each individual HAP metal.³¹ The baseline

TABLE 2-5a (Metric). NATIONWIDE BASELINE GASEOUS HAP EMISSION ESTIMATES²⁴

Gaseous HAP	Nationwide emissions, Mg/yr ^a		
	DCE recovery furnace systems		NDCE recovery furnaces
	Air-sparging BLO units	DCE recovery furnaces	
Acetaldehyde	333	769	588
Benzene	27.3	373	454
Formaldehyde	6.5	72.6	525
Methyl ethyl ketone	95.3	220	376
Methyl isobutyl ketone	39.6	312	466
Methanol	3,890	4,390	2,120
Phenol	43.3	1,020	924
Toluene	32.3	251	422
Xylenes	96.1	637	968
Hydrochloric acid	N/A	3,090	6,840
Total gaseous HAP's	4,560	11,100	13,700

^aThe emissions in this table were calculated by multiplying the emissions in Table 2-5b by 0.9072.

TABLE 2-5b (English). NATIONWIDE BASELINE GASEOUS HAP EMISSION ESTIMATES²⁴

Gaseous HAP	Nationwide emissions, ton/yr ^a		
	DCE recovery furnace systems		NDCE recovery furnaces
	Air-sparging BLO units ^b	DCE recovery furnaces	
Acetaldehyde	367	848	648
Benzene	30.0	411	501
Formaldehyde	7.2	80.0	578
Methyl ethyl ketone	105	242	414
Methyl isobutyl ketone	43.7	343	513
Methanol	4,290	4,840	2,330
Phenol	47.8	1,120	1,020
Toluene	35.6	276	465
Xylenes	106	702	1,070
Hydrochloric acid	N/A	3,410	7,540
Total gaseous HAP's ^c	5,030	12,300	15,100

^aThe nationwide emissions were calculated using the following equation:

Emissions, ton/yr = (emission factor, lb/lb BLS) x (nationwide BLS firing rate, lb/hr) x (24 hr/d) x (351 d/yr) x (1 ton/2,000 lb).

^bEmissions from the two BLO units that are controlled via incineration were multiplied by 0.02 to account for an estimated 98 percent emission reduction.

^cNumbers may not add exactly due to rounding.

PM and TRS emissions were calculated based on the sum of the PM or TRS emission rates calculated for each combustion source at each mill operating at the U.S. The baseline emissions were also calculated based on the assumption that each combustion source operates 24 hr/d for 351 d/yr.³²

TABLE 2-6. NATIONWIDE BASELINE PM, PM HAP, AND TRS EMISSIONS

Combustion source	Nationwide emissions, Mg/yr (ton/yr)		
	Total PM	PM HAP's ^a	TRS ^b
NDCE recovery furnaces	29,400 (32,400)	54 (65)	658 (725)
DCE recovery furnaces	16,000 (17,600)	31 (35)	2,720 (3,000)
Smelt dissolving tanks	7,680 (8,470)	5 (5)	7,350 (8,100)
BLO units	--	--	658 (725)
Lime kilns	8,830 (9,730)	124 (136)	648 (714)
Total ^c	61,900 (68,200)	219 (241)	12,000 (13,300)

^aOn average, PM HAP's account for 0.2 percent of total PM emitted from recovery furnaces, 0.06 percent of total PM emitted from SDT's, and 1.4 percent of total PM emitted from lime kilns.³¹

^bAs H₂S.

^cNumbers may not add exactly due to rounding.

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