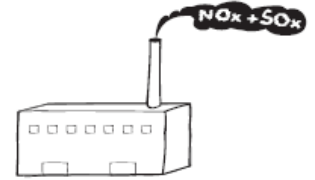


ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

A tool for understanding environmental decisions related to the pulp and paper industry



TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

Recovery Furnace NO_x

Recovery furnace (Figure S7) NO_x emissions are influenced by pulping liquor nitrogen content, combustion temperatures in the reducing zone of the furnace, and excess oxygen in the zone where most of the liquor combustion occurs.



Figure S7. Kraft Mill Recovery Furnace

Recovery furnace emissions are characterized by their high volume and relatively low concentrations of NO_x. For that reason and because of the nature of recovery furnace design and operation, viable options for further control of NO_x emissions are limited.

Kraft recovery furnaces inherently have low NO_x emissions due to a) the low nitrogen (N) concentrations in most “as-fired” black liquor solids (< 0.2%), b) low overall conversions of liquor N to NO_x by the fuel NO_x formation pathway, c) insufficient temperatures for thermal NO_x formation, and perhaps, d) the highly staged combustion design of recovery furnaces, and e) the existence of sodium fumes that might participate in “in-furnace” NO_x reduction or removal. Overall conversions of black liquor nitrogen to nitric oxide (NO) are quite low compared with other fuels, ranging from 10 to about 25% (NCASI 2003). Emission levels for individual furnaces do not vary greatly. However, there can be wide differences from one furnace to another. This reinforces the observation that each recovery furnace is an individual and that optimum conditions for process and emission performance have to be carefully sought (IPPC 2001).

Optimization of staged combustion within a large, existing kraft recovery furnace to obtain from 20% to 30% reduction in prevailing NO_x emissions is the only technologically feasible reduction measure at the present time. However, the effects of such air staging on emissions of other pollutants, mainly total reduced sulfur (TRS), SO₂, and CO, and on other furnace operational characteristics, including fouling, plugging, and chloride buildup, need to be examined with longer-term data. Lower furnace temperature conditions conducive to low NO_x formation aggravate SO_x emissions (NCASI 2003).

The panoply of other commonly cited NO_x control options can be dismissed either because they are inappropriate for the nature of recovery furnace NO_x formation or incompatible with recovery furnace chemistry and operational integrity.

What is the role of the recovery furnace in kraft pulping?

Chemical recovery is the heart of the kraft mill that allows it to operate as an essentially closed operation with recovery of spent cooking chemicals to produce fresh cooking liquor. In that process, weak black liquor from pulp washing is evaporated to between 65 and 80% solids content. The concentrated liquor is

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then burned in the recovery furnace under reducing conditions. The smelt is further processed to complete the cycle of pulping liquor preparation. See Figure S8.

The recovery furnace is often mischaracterized as a recovery “boiler” by virtue of its secondary role in also generating a significant amount of the energy required by the pulping process. It is much more than a boiler, though. It is distinguished not only because of its proportionately greater size; but most importantly, the complex chemistry that it must sustain to transform the spent pulping liquors into a reusable chemical feedstock suitable for pulping liquor production.

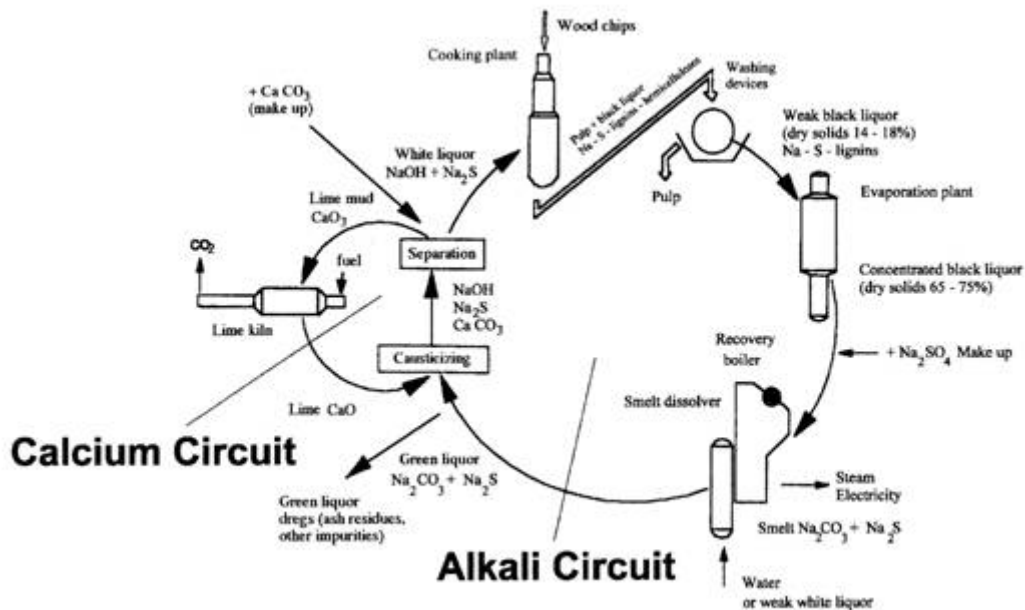


Figure S8. Kraft Mill Chemical Recovery Cycle (IPPC 2001)

What are the distinguishing features of recovery furnaces that influence NO_x emissions?

The basic elements of pulping chemicals are sulfur (S) and sodium (Na). The recovery furnace is designed and must be operated to maximize capture of these substances, as well as to separate and burn the organic substances dissolved from wood chips during pulping. The chemistry progresses through a series of complex reactions responsive to temperatures and the staged addition of combustion air that regulates available oxygen levels over the height of the furnace. The furnace environment is non-uniform.

Temperatures and oxygen-deficient reducing conditions at the base of the furnace produce molten sodium sulfide (Na₂S). Sodium fumes released in that region of the furnace react with SO₂ formed higher in the furnace, where excess oxygen levels are conducive to oxidation of H₂S that also has origins in the furnace reducing zone. Nitrogen compounds will also be liberated from the liquor in the lower furnace and, depending upon temperatures, may take a form that contributes to greater formation of NO_x in the furnace. Except for very limited circumstances, recovery furnace temperatures do not reach levels that support the oxidation of combustion air nitrogen to form NO_x. Thus, emissions of NO_x are related to the composition of the spent pulping liquor being recovered and the staged combustion conditions in the furnace.

This over-simplification of recovery furnace chemical reactions illustrates circumstances that contribute to emissions of NO_x. Other chemical reactions occur as combustion gases rise through the various zones of the furnace. The conditions under which they occur influence emissions of not only NO_x, but also odorous

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Recovery Furnace NOx

reduced sulfur gases, carbon monoxide, VOCs, and other compounds of environmental interest. The emission levels of these various substances are inter-related and cannot all be simultaneously controlled to low levels by manipulation of combustion conditions. Nor can sight be lost of the furnace's importance to the recovery of pulping chemicals. This closed-loop recycling of pulping chemicals makes it all the more susceptible to a buildup of chemical contaminants or any substances added to the liquor that deteriorate pulping liquor properties or adversely affect process equipment.

What factors influence recovery furnace emissions of NOx and the applicability of commonly cited options for their control?

Table S7b presents recovery furnace control technology options and their impacts.

Table S7b. Factors in Recovery Furnace Emissions of NOx

	NOx Impact	Other Aspects
Recovery Furnace Control Technology Option		
Increasing Black Liquor Concentration	Increased lower furnace temperatures associated with more concentrated liquor firing increase conversion of fuel nitrogen to NO. That phenomenon, combined with a possible greater tendency for the creation of thermal NOx and diminished capability for internal alkaline fume capture of NOx, results in greater furnace NOx emissions. Increasing black liquor dissolved solids content from a common 65% up to 75% may increase NOx emissions by up to 20% (IPPC 2001).	Firing more concentrated liquor increases the emissions of particulates prior to flue gas cleaning. To compensate for this, a more efficient and expensive electrostatic precipitator has to be installed. Concentrating solids may liberate sulfur compounds, requiring collection and incineration, producing SOx (IPPC 2001).
Low-NOx Burners	The highly staged combustion design of recovery furnaces, the inherent low reducing zone oxygen concentrations needed for efficient recovery of chemicals, and the dominance of temperature-sensitive fuel nitrogen precursors of NOx combine to render low-NOx burners unproductive.	
Overfire Air (OFA)	Optimizing staged combustion in the upper furnace reduces availability of oxygen for oxidation of nitrogen compounds originating in the pulping liquor. Limited short-term experience after installing "quaternary" air ports (overfire air) in two U.S. furnaces showed that a 20 to 40% reduction in baseline NOx levels is feasible. Comparable performance has been reported abroad. The practice would be limited to large furnaces (NCASI 2006). The reduction of NOx emissions is variable, dependent on the furnace type and design and the method of OFA application. It has to be adapted to the specific conditions of recovery furnaces (IPPC 2001).	The application of this technique may result in increases in carbon monoxide and unburned carbon emissions if not well controlled. The effect of such air staging on emissions of other pollutants, chiefly SO ₂ , CO, and TRS, and other furnace operational characteristics, needs to be examined with longer-term data on North American furnaces (NCASI 2006).

Table S7b. Factors in Recovery Furnace Emissions of NOx (continued)

	NOx Impact	Other Aspects
Recovery Furnace Control Technology Option		
O₂ Trim & Water Injection	Neither option is appropriate for kraft recovery furnaces since a) any injection of water into the furnace would lead to an unacceptable explosive condition; and b) the oxygen trim technique would have marginal effect due to the already existing highly staged combustion air configuration in recovery furnaces (NCASI 2006).	
Flue Gas Recirculation (FGR)	In FGR, a portion of the uncontrolled flue gases is routed back to the combustion zone, primarily with the intention of reducing thermal NOx. Recovery furnace NOx emissions are dominated by nitrogen that originates in the black liquor, not the oxidation of nitrogen in combustion air. Operational handicaps and other means for reducing fuel-related NOx erode the viability of FGR on recovery furnaces (NCASI 2006).	FGR would add additional gas volume in the furnace, increasing velocities and potentially causing more liquor carryover, which would result in increased fouling of the recovery furnace tubes (NCASI 2006).
Selective Catalytic Reduction (SCR)	The use of SCR on a kraft recovery furnace has never been demonstrated, even on a short-term basis. The impact on catalyst effectiveness of high particulate matter concentrations in the economizer region of the furnace and fine dust particles is a major impediment to the application of this technology ahead of particulate matter control. Installation after the particulate control device would render the gas stream too cold for effective reaction with the NOx. Catalyst poisoning by soluble alkali metals in the gas stream is also problematic (NCASI 2006).	Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (NCASI 2006).
Selective Non-Catalytic Reduction SNCR	Selective non-catalytic reduction (SNCR), which uses the injection of urea or ammonia into a high temperature location in the furnace, is not considered technologically feasible for recovery boiler applications because of the risk of disrupting the complex chemistry of the unit. Trials with ammonia injection in Europe indicate a 30% NOx removal capability (IPPC 2001).	Because the use of urea can eventually cause corrosion problems due to the possible formation of corrosive by-products, safety concerns discourage, if not preclude, its use in recovery boilers (IPPC 2001).
Scrubber		The scrubber requires alkali in the form of oxidized white liquor, weak liquor or sodium hydroxide, which can increase the capacity demands on other components of the chemical recovery process (IPPC 2001).

What are the trade-offs and co-benefits from recovery furnace NO_x control?

Combustion conditions inherent with recovery furnace design and operation, as well as the character of the pulping liquor fired, are influential in the level of SO_x and NO_x emissions. Altering combustion air distribution in existing recovery furnaces is capable of reducing NO_x emissions by 20% to 30% from what might otherwise be expected. That modification, however, affects process chemistry and combustion efficiency in ways that result in greater emissions of total reduced sulfur compounds (TRS), SO₂ and CO.

The firing of more concentrated pulping liquor increases lower furnace temperatures and is beneficial to reduced SO_x emissions. The temperature conditions attendant with that benefit, however, are more conducive to NO_x formation.

References

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