Air and Water Pollution Control in Crude Tall Oil Manufacture in the Pulp and Paper Industry[1]

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ABSTRACT

Pollution preventive measures should be built into the process when a new mill is designed; corrective measures must be taken on existing mills. For air pollution control, these measures consist essentially of enclosing all vessels that contain the black liquor from which the tall oil is recovered. Hoods are placed over storage tanks, sumps, heat exchangers, and other liquor-containing vessels. The hoods must be vented to a ductwork system that brings the off-gases to a central point for disposition. Typical devices to remove the offensive odors and particulate matter in the off-gases are wet scrubbers and incinerators. Evaporation can be used to concentrate liquids containing small amounts of contaminants to much smaller volumes and to concentrations that permit incineration. The lime kiln and recovery boiler of the typical Kraft mill commonly are used to burn the odorous gases, thus destroying the odors completely. Sometimes a separate incinerator is required. Water pollution is best prevented by careful design and operation of the various tall oil removal equipment, such as soap skimmers, level controls, and valving systems. In spite of great care in design and operation, some tall oil will enter the wastewater stream. The effluent treatment plant must be designed to take care of this residual biochemical oxygen demand load and, in some cases, provide for color reduction in the treated effluent.

INTRODUCTION

The general industrial clean-up program for controlling air and water pollution is having far-reaching effects in the pulp and paper industry. It involves much more than merely treating the wastewater effluents and gaseous emissions from the various areas of the mill. It has a great effect upon the economics of mill operation and the production and disposal of various by-products, as well as the incorporation of pollution control techniques in the design of processes and equipment.

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EFFECTS UPON MILL ECONOMICS

The Kraft pulp and paper industry in the Southeast operates largely upon pine wood, which has a relatively high percentage of fatty acids and rosins. These compounds react with the sodium compounds in the cooking liquor to produce a variety of sodium soaps, commonly called black liquor soap. This is a thick, sticky substance that will foul the tubes of the evaporator and create havoc with the recovery cycle–the heart of the Kraft paper-making process. In most mills, this soap is collected at convenient points and removed from the liquor for processing. In general, there are two basic approaches to the utilization of soap: (a) sell the soap to a tall oil processing plant that recovers and distills the tall oil that the soap contains, and (b) install a tall oil plant at the mill and prepare a crude grade of tall oil for sale to users. Most mills have found the latter approach more attractive economically. Both approaches have drawbacks, as well as advantages.

If the soap is sold to a tall oil plant, the mill loses the heat value of the lignin, ordinarily separated during crude tall oil manufacture, plus a considerable quantity of sodium that can be recovered in the recovery boiler when the tall oil wastes are burned (Fig. 1). The sodium lost is replaced by purchasing salt cake. On the plus side, however, is the outright elimination of a problem: what to do with the by-product brine. As a discharge into a plant wastewater stream, it creates an increased biochemical oxygen demand (BOD) and chemical oxygen demand (COD) load, thereby requiring a more expensive and extensive waste treatment plant.

If the mill elects to install a tall oil recovery facility, the tall oil is removed from the soap (Fig. 2) and sold at a higher price than the soap. This price difference is about \$12/ton crude tall oil. The mill, of course, has to maintain and operate the tall oil plant and has to decide what to do with the residuals left over from the tall oil plant. Here again, the mill is faced with a decision based upon technical problems vs. the economics of mill operation. Captial investment for tall oil plant in a 1000-ton pulp mill will be ca. \$500,000; operation and maintenance will be \$130,000/yr. Therefore, it is not generally feasible to install a crude tall oil plant in a mill with less than 600 tons/day of

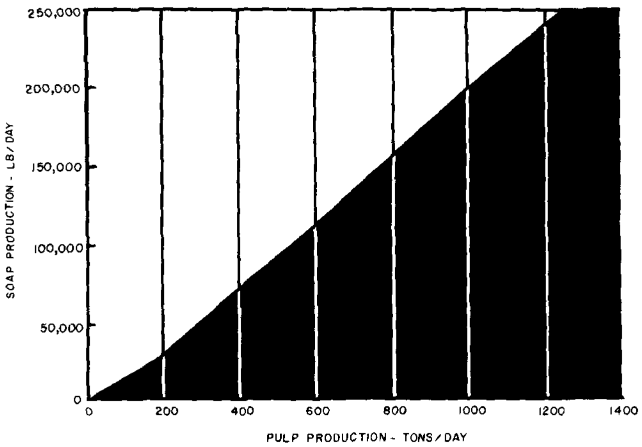

FIG. 1. Soap production–average southern Kraft pulp mill.

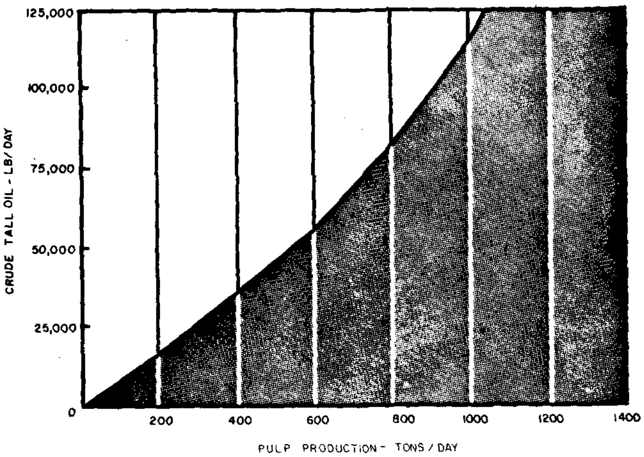

FIG. 2. Crude tall oil production where pulp mill has acidulation plant.

pulp production, because the cost of processing the soap would exceed the return from the sale of tall oil.

PROCESS APPROACHES

The typical paper mill tall oil plant uses sulfuric acid to break the sodium bonding to the fatty acid and rosin acid radicals. This reaction produces sodium sulfate and releases fatty acids and rosin acids. The acidulated material rises to the surface where it is skimmed off and pumped to storage as crude tall oil. The mill's problem, at this point, then is how to handle the rest of the black liquor residual. This residual liquor consists of two basic components, lignins in solution as an upper layer (sp gr ca. 1) and sodium sulfate (brine) in solution as a lower layer (sp gr ca. 1.3). The separation is rather imperfect. The practice of handling the liquor varies in different mills (1).

Some mills pump the entire mixture to the black liquor stream, where it is eventually burned in the recovery boiler. The sodium compounds are recovered; however, the sulfur compounds also are recovered, and these have a tendency to build up the sulfidity in the mill's recovery cycle. This creates additional odor control and corrosion problems that must be corrected. The brine is highly corrosive and may cause damage to the boiler. This may be even more of a hazard in bleached pulp mills; these mills may use spent acid from their ClO_2 generator to furnish part of the acid requirements for soap neutralization. This spent acid is notoriously corrosive. Violent agitation must be used where this spent acid is added to the black liquor to disperse completely the acid in the receiving liquor. Otherwise, corrosion will occur.

Other mills make the separation into lignins and brine, imperfect as it is, and do the best they can with the separate fluids. The lignins can be cooked with white liquor, usually on a batch basis, when enough lignin has accumulated for a reasonable batch. The cooked lignins and spent caustic then enter the recovery cycle through the black liquor stream. The lignins are burned in the recovery boiler, and the caustic is recovered. When this method is used, the brine fraction is discharged into the wastewater stream and treated in the wastewater treatment plant.

EFFECTS OF NEW WATER POLLUTION CONTROLS

This brings us to the problem that many mills now are facing. The tightening of standards on waste discharges and the enforcement policies now prevalent have caused many mills to reexamine their position—both economically and from the technical standpoint. They are exploring every possible way to reduce the quantities of effluent. Many are exploring new techniques for treatment of the wastes. They are hard pressed to meet the new codes with their tall oil plants in operation. They are beginning to ask whether it is still economically preferable to operate a tall oil plant and the attendant more extensive treatment plant or to return to the former practice of selling the soap and replacing lost chemicals. If they do, indeed, choose the latter course, it will place the process problems in the hands of the oil chemists. They then will have far more black liquor soap available to be processed into tall oil. They also will have to solve the waste treatment problems at the tall oil plants.

The treatment system for a tall oil plant's wastewater uses the same basic chemistry as the tall oil processing itself. The wastewater is treated with sulfuric acid to release the residual tall oil and effect a separation based upon specific gravity. The tall oil is skimmed from the surface, and the remaining liquor then is treated for its high BOD load, much the same as other pulp mill wastewaters are handled.

One approach is to add ferric chloride to the waste liquor for its coagulating effect (ca. 200 ppm). NaOH is used to adjust the pH to ca. 6.5. After these chemicals are mixed thoroughly with the waste liquor, the waste liquor is allowed to settle. The lignins and other solid constituents will settle to the bottom of the vessel. The clarified effluent then can be pumped to an effluent stream for disposal, sometimes through a filter to help remove any solids in suspension. The settling basin, of course, has to be cleaned periodically to remove the settled solids. Most systems will have two basins, one for use while the other is being cleaned. The sludge deposits generally are hauled to an off-site landfill.

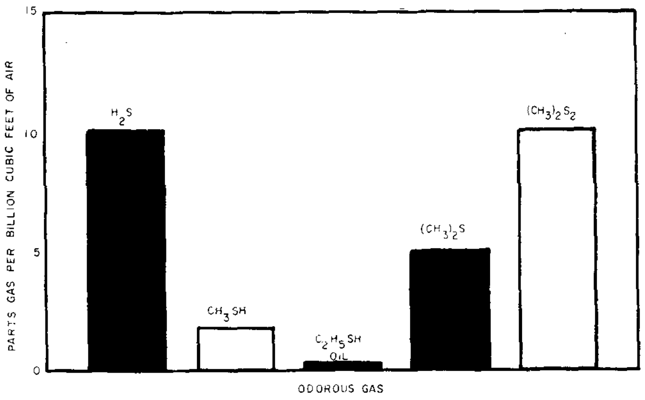

FIG. 3. Odor threshold of various pulp mill gases. SO_2 varies from 400-3,000 ppb.

To summarize the present day situation, we find that, in a 1000 ton/day unbleached pulp mill with a typical crude tall oil plant, the brine and lignin (if both are added to the waste sewer) will increase the BOD load to the waste treatment area by ca. 80% of the initial total BOD. Furthermore, the dissolved solids leaving the mill will increase ca. 30,000 lb/day as Na_2SO_4. The increased BOD can be handled generally in a modern waste treatment facility by additional aeration in the secondary lagoon or pond. The dissolved solids (inorganic salts) pose a very real problem to the waste treatment chemists. If treatment has to be added for reducing these, then the economic advantage of the conversion of soap to crude tall oil would disappear quickly. The added investment in a 1000 ton mill for aeration would be ca. $20,000, plus $10,000/yr operating and maintenance cost, but the cost of the removal of the added dissolved solids as Na_2SO_4 would be considerably higher.

AIR POLLUTION PROBLEM

The air pollution problem in a tall oil plant generally is confined to the emission of H_2S. The sulfur-bearing gases, such as H_2S, are released during the cooking process. These compounds have a low odor threshold, as can be seen from Figure 3. They are all below 10 ppb, as compared with SO_2, which has an odor threshold that varies from 400-3,000 ppb (2). These odors are referred to as total reduced sulfur (TRS) and generally are given in ppm on a volume basis as dry gas equivalent to hydrogen sulfide, or, more simply, they are called TRS as H_2S. The average 1000 ton/day pulp mill cooking pine wood may emit as much as 25,000 lb TRS/day, if no attempt is made to control this odor (3). The largest single contributor would be the recovery furnace. In theory, it would contribute 70-80% TRS. The modern mill now is installing new low-odor boilers that will reduce TRS from the recovery boiler down to 250 lb/day; and, if no other process in the mill were treated, the 1000 ton/day pulp mill then would emit only 5250 lb/day TRS. If we also control odor by incinerating the gases from the digesters, evaporators, and turpentine condenser, the total odor emission would be reduced to 2500-3000 lb TRS/day. If there is a tall oil plant in the mill, 1200-1500 lb/day TRS would be emitted from this source. Since this is 50% of the remaining emission from the plant, it becomes necessary to treat TRS emission from the tall oil plant.

ODOR CONTROL METHODS

This odor is primarily H_2S emitted from the soap mixture, when acid is added to the reactor. It can be scrubbed down to a low level using caustic soda. Scrubbers have been used with fiber glass reinforced polyester (FRP) construction and polypropylene packing to remove as much as 99.9% H_2S.

If the tall oil plant is a batch system, there is usually a large reactor in which the acid and soap are mixed together. Generally, steam is added to the mixture to give enough heat to increase the efficiency of the reaction, since the soap is viscous at ambient temperature. This evolves great quantities of vapor which contain the odor-bearing gases. We have found that, in this system, a fan of ca. 5000 ft^3/min capacity will be required, and we think it is best to make it an induced draft type, i.e. it is installed after the scrubber and exhausts to the atmosphere or to an FRP stack. The scrubber can be a packed bed type or a Venturi, but it should be of fiberglass construction, that is FRP material, such as ATLAC 382 or Hetron 92. The ductwork and scrubber should be of the same material. If a Venturi is used, an entrainment separator of FRP material will be required also. Spray nozzles should be Carpenter 20 alloy. A 5 or 10% NaOH solution should be used in the scrubber. The solution can be used once through or be recirculated.

Often there is white liquor available in a pulp mill. This consists of ca. 10% NaOH solution with 2% Na_2S present. It is not as efficient as 10% NaOH without the Na_2S; but, since it is readily available in the mill, it often is used as the scrubbing medium. It must be cooled before it can be used as a scrubbing solution. Generally, we install a simple water-cooled heat exchanger for this purpose. Mill water, at ca. 90 F in the South, is used to cool the white liquor down to 100 F for scrubbing. The caustic then is fed into a sump or pump suction tank by level control. A portion of the recirculating scrubber solution is bled off by a circulating pump discharge header to the white liquor storage tank in the caustic area. A flow controller is used to regulate the flow to the storage tank. If the pulp mill has a bleach plant, 5% NaOH solution is generally available. The caustic solution does not contain Na_2S and makes a better scrubbing medium. The caustic solution then is piped into the white liquor system after scrubbing the tall oil gases.

If the mill has a continuous tall oil reactor, instead of a batch system, the problem of air emission is somewhat different, since the emissions are more dilute and require a larger ventilating system. Generally, a centrifugal separator follows the continuous reactor, and it is in the same building as the reactor (4). The building must be ventilated and probably would require 10,000-15,000 ft^3/min air movement. This air would be passed through a packed bed scrubber (low head loss) to minimize the horsepower.

The caustic scrubbing medium would be the same, except that it could be recirculated a lot longer, because the H_2S pickup would be lower/hr.

In both types of plants, there will be soap storage tanks, lignin or spent liquor tanks, brine tanks, tall oil storage, and maybe a drying tank or dehydrator system for drying the tall oil before shipment. All of these tanks should be vented to the odor control system of the pulp mill. Generally, in a modern mill, this would consist of a large gas holder, ductwork, and fans to pick up odors from throughout the pulp mill and incinerate these odors in a separate gas-fired incinerator, lime kiln, or recovery boiler.

The actual lb/day TRS from a tall oil plant are not much, but they carry such a high odor intensity that it becomes very important to achieve a high order of efficiency for removal of these odors. The public today equates odor with air pollution, so we must recognize this in our design efforts.

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