ENGINEERING PROBLEMS ENCOUNTERED

IN THE RECOVERY

OF

PAPER MILL BY-PRODUCTS

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Sulfate turpentine and tall oil, both by-products from the pulp and paper industry, are among the most versatile chemicals used by man. Turpentine is used in a wide variety of products, some of which are: Cleaners, disinfectants, solvents, insecticides, vitamins, resins and perfumery and flavoring compounds. Tall oil is used in such products as: Resins, synthetic lubricants, plasticizers, detergents, soaps, surfactants, dispersing agents, pharmaceuticals, paper size, paints, varnishes, printing inks, fungicides and flotation agents.

Turpentine and rosin were first obtained by tapping the living pine tree. The rosin and pitch compounds obtained were extensively used in sailing ships for caulking seams and treating ropes - hence the term "naval stores". The first shipment exported from what is now the United States was a cargo of naval stores in 1608. Earlier, in 1584, Sir Walter Raleigh's colonists reported that there were "trees which could supply the English Navy with enough tar and pitch to make our Queen the ruler of the seas". In 1670 the General Count of Massachusetts established a monopoly for the purchase of naval stores, the first recorded monopoly in this country. The first conservation legislation in America was passed in Massachusetts in 1715, requiring a permit to cut pine trees or de-bark them for gum collection. Another indication of the importance of the pine tree to the colonists is that the first American coins were the pine tree shillings of Massachusetts. Even the early American flags showed the pine tree on them.

Although the naval stores industry originated in New England, the large southern forests and cheaper labor caused a gradual shifting to the South. In 1840 North Carolina boasted 1526 naval stores plants. New uses were being discovered for turpentine and rosin. In 1863 confederate surgeon Francis P. Porcher described the long leafed pine of the South as "one of God's great gifts to man". He reported turpentine and pine tar widely used as medicinal agents as an external rubefacient, a stimulant, an astringent, a stimulating diuretic and laxative and in addition, an excellent way of chasing away fleas.

The Civil War slowed down the development of the naval stores industry for only a short time. By the turn of the century, new processes were developed, as evidenced by the number of patents issued during that time. Savannah and Jacksonville became major shipping ports for the export of naval stores. By the mid-twentieth century, increasing labor costs and decreasing stands of virgin forests brought a slow but steady decline in the gum naval stores industry. During this period, researchers and engineers paid more and more attention to the recovery of turpentine and tall oil as by-products of the pulp and paper industry.

In the pulp and paper industry, sulfate turpentine comes off in the early stages in the cooking cycle of the digestion of wood chips. Tall oil comes off in the evaporation of black liquor as soap, which rises to the top of the soap skimmer where it is separated by skimming, and later acidulated to crude tall oil. For many years these by-products were given low priority by the paper mills and were either not recovered or poorly recovered and burned for fuel. As their versatility was recognized and demand increased, steadily rising prices have caused the paper mills to take an active interest in the recovery of these by-products.

I would like to go over some of the engineering problems and solutions encountered in the recovery of these by-products. We will discuss turpentine first and then tall oil.

Although recent discoveries have shown methods of greatly increasing the amount of oleoresin in the living tree, laboratory studies have shown that half or more of the turpentine content of the tree is lost before the wood chips are even put into the digester. Methods of reducing this loss include spraying the wood with water or chemical solutions, storing as roundwood instead of chips and rotating the wood pile so as to optimize the percentage of fresh wood fed to the digesters.

In the batch system, the digester is continually vented during the cooking cycle to allow air and noncondensables to escape. Experimental vent relief studies, using a pilot turpentine recovery system attached to vent line of a single digester, showed that turpentine is distilled over from about 40 psig to cooking pressure of 100 psig. This experimental work showed the importance of venting or "gassing off" the digester properly to optimize turpentine recovery. If the vent relief line is not properly controlled, then cooking liquor, and even fiber, can be carried over causing problems in the separator, condenser and decanter. Also substantial steam savings can be obtained with controlled venting. The results of these tests have been the establishing of a venting profile for maximum turpentine recovery and reduced steam usage through the use of control valves on the digester vent lines, some of which are computer controlled.

The vent lines from all the digesters go to a header which goes to a separator, the function of which is to separate black liquor carried over from the steam air, noncondensables and turpentine vapor. In many cases, poor turpentine recovery is due to such things as (1) uninsulated header lines and separators, (2) an inadequate seal leg (less than the pressure drop in the condensers) and (3) poorly sized or designed separators. It is essential that the separator remove all entrained black liquor since black liquor coats the tubes of the condenser lowering the heat transfer coefficient and tends to emulsify the water-turpentine mixture in the decanter.

The typical separator found in a paper mill is the cyclone separator, primarily designed for solid-vapor separation. A better separator design is the inverted cone, wet wall separator. This separator uses pressure gradients to develop an effective centrifugal force during the helical flow of gasses through the separator. The deposition of liquid droplets in a wall film permits the effective separation of liquid from the vapor.

Vapor from the separator goes to the condenser where steam and turpentine are condensed and air and noncondensables are vented.

Most paper mills have one or more large condensers, usually designed for other uses, mounted vertically with little or no attention paid to how it is cooled or vented. Experimental work has shown several improvements in the design and operation of turpentine condensers. A horizontal condenser gives a better overall heat transfer coefficient and allows easier removal and cleaning of the tube bundle. By operating the condenser hotter than usual, 150-160^{o}F, improved turpentine recovery is obtained in the decanter. This is because the solubility curve for turpentine and water is inversely proportional to temperature, at a higher temperature there is less tendency for emulsion and there is a slightly increased spread in the densities of turpentine and water, all of which improve the separation of turpentine and water in the decanter.

Because the condenser and decanter are operated at a higher temperature, it is necessary to install a scrubber on the combined vents with the underflow returning to the decanter. This also reduces pollutants to the air. Incorporated into the design of the condenser is a cooling water recirculating system which provides a constant hot water discharge temperature for other uses in the mill and a constant water velocity in the tubes. The horizontal decanter is preferred to the usually found vertical one so as to give a longer horizontal travel for both water and turpentine and a shorter vertical travel for better separation. Since the decanter is warmer than usual, the turpentine is cooled before entering the storage tank by a water-jacketed subcooler. The storage tank must be kept full at all times to prevent vapor phase corrosion.

In the continuous Kamyr digester system, poorer turpentine recovery is encountered, about 45-50% of that from the batch digester. The difference in yield between the batch and Kamyr systems is due to process differences as follows:

(1) In the Kamyr system there is no vapor space at the top of the digester, permitting the removal of turpentine and noncondensables in the early part of the cook as the turpentine is formed. Instead, turpentine must be removed from the black liquor following the cook at the time when turpentine is more soluble in the organic solids that are formed in the cooking process.

(2) The turpentine-to-water ratio is much higher in the Kamyr system, in the range of 50 or 100-to-1 compared to a batch system ratio of 10-to-1.

(3) There are three to four times as much noncondensables, mainly air, in the Kamyr system which must be removed in the turpentine recovery system, as compared to the amount of noncondensables in the batch system.

(4) Most of the Kamyr turpentine recovery systems were not designed properly, particularly in the cases of items 2 and 3 and appear to have been designed as if the system operated like a batch system.

Since part of the turpentine does not get to the turpentine recovery part of the Kamyr system, other methods must be used to improve turpentine recovery. One method is to take off part of the vapors in the black liquor evaporators and condense out the turpentine and return most of the steam to the system. On one mill having a flash evaporator system using this concept, an additional 20-30% of the turpentine was recovered. A West Coast mill installed a vaporsphere to collect and condense all vapors, added condensers to the filtrate tanks and added a scrubber to its evaporator hot well and has improved its overall recovery to about 60%. Another method is to direct the steam from No. 1 flash tank to the recovery system instead of to the steaming vessel, but it is doubtful if it is economically feasible. There is also a Russian patent for venting gases and vapors from the external circulating heating systems of the Kamyr digester. Some improvement in the Kamyr system can be accomplished by proper design of the overall turpentine recovery system in view of the difference between it and the batch system. This may involve such things as the installation of a separator to correct foaming and liquor carryover from the flash tanks, improving the operation of the flash tanks and increasing the size of the condenser and decanter. There is still much work to be done on improving turpentine recovery in the Kamyr system.

In the area of improving tall oil recovery, there have been several significant improvements. Mill surveys show that only about one half of the tall oil content of the wood chips fed to the digester is recovered as crude tall oil. The first step is to analyze various streams in the mill and make a tall oil material balance. The biggest loss occurs in the wood storage area and the same methods of decreasing the length of time fresh cut wood is kept in storage, will improve tall oil, as well as turpentine recovery.

In the cooking step, the addition of small amounts of cooking aids such as N, N-dimethylamides of tall oil fatty acids have been shown to reduce cooking time, increase pulp yields and reduce the loss of tall oil left in the washed pulp. In many mills poor pulp washing results in losses of tall oil as high as 25 pounds of tall oil per ton of pulp. A washing aid, such as the addition of 6-7 grams of propyl stearamide per ton of pulp has been shown to reduce the tall oil in the washed pulp and also improve soap separation in the skimmer.

Mills that report the highest tall oil yields are also the ones that operate their weak liquor (evaporator feed) tanks at a higher than usual (17% vs 14%) solids content and also skim soap from the weak liquor tanks. Some mills collect as high as 60% of their tall oil by this method. Tests have shown that soap collected here results in a higher quality tall oil.

The principal collection point for tall oil soap is from a skimmer located in the multiple effect black liquor evaporaters at a point where the black liquor has been concentrated to about 25% total solids. Some of the parameters affecting tall oil soap recovery in the skimmer are: Total solids concentration, retention time, temperature, composition of the tall oil, pH, sulfidity, hardwood to pine liquor ratio and configuration of the skimming vessel. Several studies have been made on the effects of these variables.

One result of these studies showed that most skimmers were poorly designed. A skimmer should have the following features for maximum efficiency:

(1) There should be a minimum of short circuiting, assured by proper baffling.

(2) There should be a minimum distance for the soap to rise to the surface for collection.

(3) There should be minimum turbulence.

(4) There should be no areas in the tank where the downward movement is greater than the velocity of rise of soap particles in black liquor (which is about 2.5 feet per hour for most soap particles).

(5) Retention time should be sufficient to give the soap time to rise to the surface.

Another study showed that the addition of 0.5 to 1.0% by volume of certain medium boiling aromatic solvents immiscible with the liquor caused the rapid agglomeration of small diameter soap particles that are normally not recoverable. The addition of a small flow of air to the skimmer feed along with the solvent makes it possible to recover all of the suspended soap in a single skimming operation.

The small soap particles can also be agglomerated by immersing direct current electrodes into a stream of black liquor containing black liquor soap. Low voltages are desirable for the best separation and to prevent the breakdown of water to hydrogen and oxygen. A small pilot skimming unit has been built and operated in the mill to optimize tall oil production by studying many of the above mentioned variables.

Most mills at the present time use the batch acidulation system for acidulating their soap to crude tall oil. A new continuous acidulation process has been developed which includes a counter-current washing step to reduce the liquor content of the soap giving an increased tall oil yield.

Improved recoveries of both turpentine and tall oil offer real challenges to the chemical engineer. Not only can significant losses be reduced and subsequent revenues increased, but contributions can also be made to pollution abatement. The application of basic chemical engineering principles and small capital expenditures can show immediate returns.

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