THE BASICS OF FOUL CONDENSATE STRIPPING

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ABSTRACT

Foul condensates from the digesters and evaporators contain reduced sulfur gas and organic compounds, such as methanol (MeOH) and turpentine, which contribute greatly to pulp mill water pollution in the form of Biochemical Oxygen Demand (BOD) and toxicity, and air pollution in the form of Volatile Organic Compounds (VOC), and odor.

For this reason, foul condensates are collected and treated by stripping, using either air or steam, to remove the pollutants. In many cases, the pollutants can be economically used as a fossil fuel substitute.

This paper will cover the condensates that are collected, various stripping methods, types of stripping columns, basic theory, operating problems, the latest operating procedures, and disposal of the stripper off gas (SOG) which contains the pollutants removed.

INTRODUCTION

The Cluster Rules resulting from the Clean Air Act Amendments (CAAA) of 1990, will require the collection and treatment of "Kraft process condensates", better know as foul condensates or combined condensates.

Steam stripping is one of the treatments accepted by the Environmental Protection Agency (EPA). The others are hard piping to biological treatment, reusing the condensates in a process where the vents are collected and incinerated, or any other process that can meet the required removal efficiencies.

Although the rules allow various methods of determining removal efficiencies, bleached mills will have to collect selected condensates and treat them to destroy 10.2 pounds of methanol (MeOH) per oven dry ton of pulp (ODTP) (5.1 kilograms per oven dry megagram of pulp). Unbleachedmills will have to destroy 6.6 pounds per ODTP (3.3 kg/Mg).

Most mills built or upgraded since 1980 have had a condensate stripping system installed as an integral part of the overall mill process. Many older mills have now added a foul condensate stripper to meet the new EPA Cluster Rule.

Table I Typical Pollutant Loads in Foul Condensates
Bleached Kraft Mill
Based on Unbleached Digester Production

Source	Total Flow		MeOH		Turpentine		TRS	
	kg/tonne	lb/tonne	kg/t	lb/t	kg/t	lb/t	kg/t	lb/t
Batch Digester Mill (Softwood)								
Digester accumulator overflow	1125	2250	4.0	8.0	0.50	1.0	0.20	0.40
Turpentine decanter underflow	250	500	1.5	3.0	0.50	1.0	0.15	0.30
Total evaporator condensate	7000	14,000	4.2	8.4	0.25	0.5	1.00	2.00
Continuous Digester Mill (Softwood)								
Turpentine decanter underflow	450	900	2.5	5.0	0.50	1.0	0.12	0.24
Total evaporator condensate	8000	16,000	7.5	15.0	0.50	1.0	1.20	2.40

WHY STRIP FOUL CONDENSATES?

The prime reason for stripping foul condensates is pollution control. Foul condensates can contain 14 to 20 lb (7 to 10 kg) of BOD, 2 to 4 lb (1 to 2 kg) of turpentine and 2 to 4 lb (1 to 2 kg) of TRS per ton (tonne) of pulp (Table I).

If these foul condensates are untreated, they cannot be reused in the mill and are therefore sewered, putting a high load of BOD and toxicity into the secondary treatment system and frequently causing air pollution problems, as the TRS and MeOH is released to the atmosphere by flashing off from open sewers.

By collecting these foul condensates and stripping them, most of the pollutants can be removed and burned, reducing the pollution load to the air and to the secondary treatment system.

In most cases, the stripped condensates can be reused in the mill for such purposes as brown stock washing and make-up water in the recaust area. Thus, stripping also has the potential to reduce the total mill water demand. Stripping will also be an integral part of the effluent free mill of the future.

Fortunately, the stripped compounds are easily burned. Heat of combustion values for stripper overheads in the order of 120,000 Kcal/tonne (475,000 BTU/Ton) pulp have been reported (Table II).

These stripper overheads can be transported as a gas, or condensed and transported as a liquid and used to replace fossil fuel in lime kilns, boilers and incinerators. In most cases, the net heat released by burning these pollutants is greater than the heat energy required to operate the stripper, and can be used to help economically justify installing the stripping system.

Table II Heat Value of Pollutants

Pollutant	Net Heat of Combustion	
	kgcal/kg	Btu/lb
MeOH	5037	9066
Alpha-pinene	9547	17,200
H_2S	3647	6565
CH_3SH	6229	11,212
CH_3SCH_3	7371	13,268
CH_3SSCH_3	5638	10,148

WHAT CONDENSATES ARE STRIPPED?

The Cluster Rule requires collection and treatment of the condensates from the digester system, the turpentine recovery system, the evaporator systems, the HVLC (dilute NCG) collection system, and the LVHC (concentrated NCG) system.

Batch Digester Blow Steam Condensate

The condensates from condensed blow steam are rich in methanol and TRS. In order for these pollutants to be collected, however, the blow steam system must function correctly. If the blow steam system is undersized or operated incorrectly, much blow steam is vented with much of the methanol and TRS vented as well.

In some mills, fresh water is added to the accumulator to keep the bottom temperature low. This dilution of the blow steam condensate makes collection of these condensates undesirable.

In a modern blow steam condensing system, the direct contact primary condenser is followed by an indirect secondary/tertiary condenser. It has been found that up to 80% of the pollutants can be "segregated" into the 10 - 15% of condensed blow steam that comes from the secondary/tertiary condenser. This concentration of the pollutants in a smaller flow greatly improves the efficiency and economics of stripping.

The Cluster Rule will allow the treatment of only the segregated stream, provided that at least 65% of the methanol in all the blow steam condensates is contained in the segregated stream.

Batch Digester Relief Steam

During the cook, non-condensable gases (NCG) are vented from the digester. The NCG contains considerable amounts of steam, MeOH, and frequently turpentine. This steam must be condensed in order to collect the NCG. The condensates so formed must be collected and treated. As above, this condensation can be done in two stages, and only the rich or segregated stream collected and treated, providing at least

65% of the methanol in the relief gas is in the segregated stream.

Continuous Digester Flash Steam

During the cook, hot, pressurized liquor is removed from the digester and flashed to atmospheric pressure. The flash steam contains considerable amounts of NCG, MeOH, and frequently turpentine. This steam must be condensed in order to collect the NCG. The condensates so formed must be collected and treated. As above, this condensation can be done in two stages, and only the rich or segregated stream collected and treated, providing at least 65% of the methanol in the flash steam is in the segregated stream.

Turpentine Decanter Underflow

In softwood mills, batch digester relief steam condensates and continuous digester flash steam condensates go to a turpentine recovery system. The underflow from the turpentine decanter is a relatively low flow that is rich in methanol, turpentine and TRS, making this foul condensate a prime candidate for stripping.

Evaporator Condensates

The combined foul condensates from the multiple effect evaporators contain methanol, turpentine and TRS removed from black liquor during evaporation. The evaporators, in effect, act as strippers to remove these pollutants from the black liquor.

It has been found that most of the pollutants (80%+) will collect in the condensates of the effects and condensers following the effects where the weak black liquor is fed. For example, if weak black liquor is fed to effects 5 and 6 of a six-effect evaporator, the pollutants will be found in the condensates from the 6th effect and the surface condenser. The Cluster Rule will allow splitting out such condensates for treatment, thus reducing the amount of evaporator condensate to be treated by about two thirds.

In modern multiple effect evaporators, especially those of the falling film design that have been supplied since 1980, the majority of the pollutants can be collected in 15% or less of the total condensate. This is primarily done by using two-stage condensing with internal condensate segregation. This, as mentioned above, greatly reduces the condensate to be treated, and thus improves the efficiency and economics of stripping.

In general, there will be four condensate streams generated in a modern falling film evaporator. The first is clean steam condensate from the first effect. The second is combined condensates from the middle effects, and these will have methanol in the 100 ppm range. The third stream is contaminated condensates from the lean steam of segregated condensates from the feed effects, and these will have methanol concentrations in the range of 1000 ppm. The final stream is foul condensates from the rich stream of segregated condensates, and the methanol will be in the 5000 ppm range.

The Cluster Rule will allow segregation of condensates, providing that 65% or more of the methanol in all the evaporator condensates is in the segregated stream.

NCG System Condensates

The condensates formed in NCG systems, although small in volume, are very concentrated in methanol and TRS compounds, and contribute to odors in the mill area if drained into open sewers. The Cluster Rules may require collection and treatment of these condensates.

METHODS OF STRIPPING

There are two methods of stripping used in Kraft pulp mills today. One uses air and the other uses steam. Both of these methods can be further subdivided into two types of strippers; stripping for TRS only and stripping for methanol (BOD). TRS is easily stripped, whereas MeOH is more difficult, consequently making the latter systems bigger and more complex. Further, the new Cluster Rules will not accept air stripping, or stripping for TRS only.

Air Stripping for TRS

This is the most basic form of stripping and is generally used to remove TRS from condensates so that they do not create odor problems in the secondary treatment system (Figure 1). In this case, the foul condensates are stripped by air moving counter-currently in a stripper column.

About 3 - 5 weight % of air on condensate is required. Higher air ratios may be necessary if

the TRS concentration is high, in order that the stripped gases are well below the Lower Explosive Limit (LEL) in the overheads.
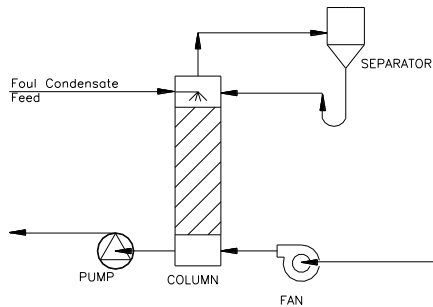

Figure 1. *Air Stripper for TRS*

The two factors which have the greatest effect on air stripper efficiency are temperature and pH (Figure 2). A pH of seven or less and a condensate temperature of 50 °C (120 °F) or more are required for good stripping efficiency. Disposal of the high volume of warm moist overheads is the major disadvantage of this system.

Disposal is usually done by burning in a boiler, kiln or incinerator. The major advantages of this system are its simplicity and low cost.
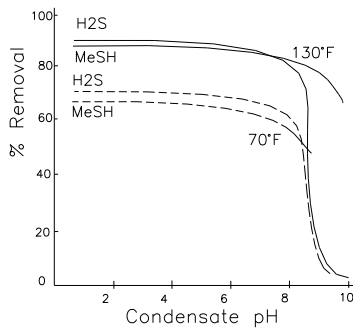

Figure 2. *Air Stripper Eficiency*

Air Stripping for BOD

This system is similar to air stripping for TRS, except that much higher quantities of air are required, in the range of 16 - 20 weight % air on condensate. Temperature is also very important and temperatures in excess of 70°C (160°F) are required for good efficiency. This form of stripping is not practical, and is not practiced.

Steam Stripping for TRS

This system is similar to the air stripper except that two heat exchangers are added to the system (Figure 3). It is necessary to preheat the foul condensate before stripping, otherwise the stripping steam would be condensed by the cold condensate. This preheating is done by heat exchanging with the hot stripped condensate.

The second heat exchanger is used to condense the steam out of the stripped TRS gas before it is incinerated. The condensate is returned to the top of the stripping column. About 3 - 5 weight % of steam is required on condensate.
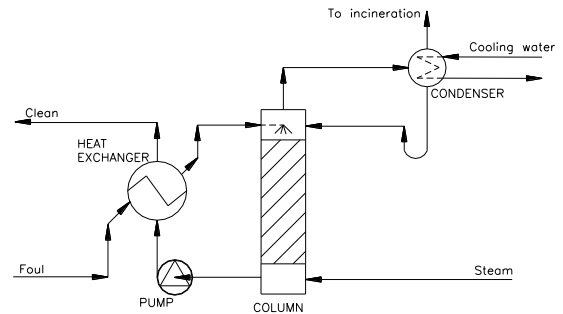

Figure 3. *Steam Stripper for TRS*

As with air stripping, efficiency is pH dependent. Despite the disadvantage of higher capital and operating cost, disposal of the overheads is much simpler. Operating costs can be reduced if some use can be made of the hot water generated in the overhead condenser.

Steam Stripping for BOD

This system is similar to the steam stripper for TRS except that the overhead condenser becomes a reflux condenser and the top of the column becomes a distillation column to concentrate the methanol (Figure 4).

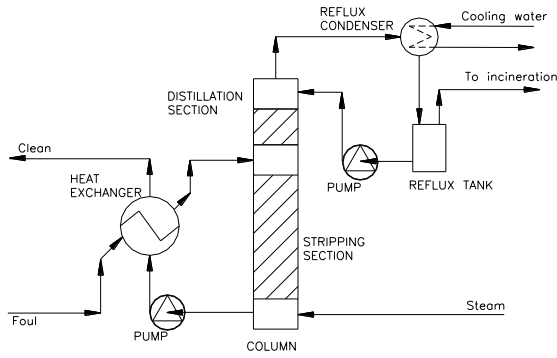The steam requirement increases to 15 - 20 weight % steam on condensate (Figure 5).

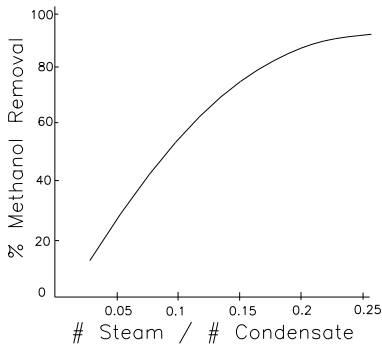**Figure 4**. *Steam Stripper for B.O.D.*

Figure 5. *Distillation Efficiency*

These systems have the advantage of high efficiency, producing an overhead that is usable as a fuel. The major disadvantages are high capital and operating costs. The operating costs can be reduced if some use of the heat from the reflux condenser can be found such as preheating boiler feed water, or making clean hot water for a bleach plant.

The reflux tank shown in Figure 4 is optional, and many systems do not have them, Instead, the reflux condenser is positioned above the column, and reflux flows by gravity back to the column.

There are examples of this type of stripping system at the mills in Palatka, FL., and Brunswick, GA.

TYPES OF COLUMNS

In general, two types of columns are used for stripping; packed columns and valve tray columns.

Packed columns are generally cheaper, especially for small diameter columns. Packing material is either stainless steel pall rings or corrosion

resistant plastic saddles. The disadvantages of packed columns are poor turndown ratio and plugging of the packing by fibers carried in the condensate.

Valve tray columns are an advanced form of a bubble cap tray column. They have the advantages of maintaining high efficiency over a wide operating range, a constant pressure drop at varying vapor load rates and self-cleaning of the trays. These advantages normally offset the higher capital cost of the valve tray column.

As a general rule, packed columns are used for TRS strippers and very small BOD strippers, while valve tray columns are used for large BOD strippers. The valve tray column has become the standard under the Cluster Rule.

INTEGRATED COLUMNS

In order to reduce the capital and operating costs of steam type BOD strippers, they are normally integrated into a set of multiple effect evaporators. There are two basic ways to do this.

Fully Integrated

The stripping column is placed between two effects, usually the No. 1 and No. 2. Steam from the No. 1 effect is run through the stripper and then condensed in the No. 2 effect. The No. 2 effect is the reflux condenser, saving this capital cost. The stripping steam is essentially free.

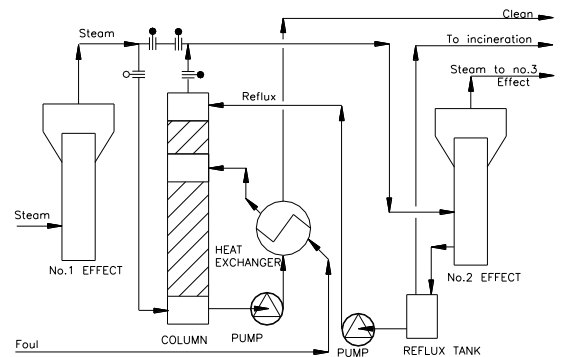Figure 6 is a schematic depicting a fully integrated stripping system.

Figure 6. *Fully Integrated Column*

However, there is an efficiency loss of about 12% in the evaporators when the column is fully integrated. In a system of this type, for every Kcal or BTU lost by integration, two or more Kcals or

BTUs are returned by the heat value from burning the stripped BOD.

This type of full integration with respect to the evaporators can be used when a stripper is integrated into an existing mill, and where condensate flows are high compared to the relative size of the evaporators.

Partially Integrated

In the case of a new mill with reduced foul condensate flows, and where the stripper is part of the initial evaporator design, only partial integration is required.

In this case, only part of the evaporator steam flow is used for stripping and the overheads are condensed in either an external preheater or in a dedicated internal section of a subsequent evaporator effect. Such systems have a much better energy return than fully integrated systems.

There is an example of this type of stripper at the mill in Leaf River, MS.

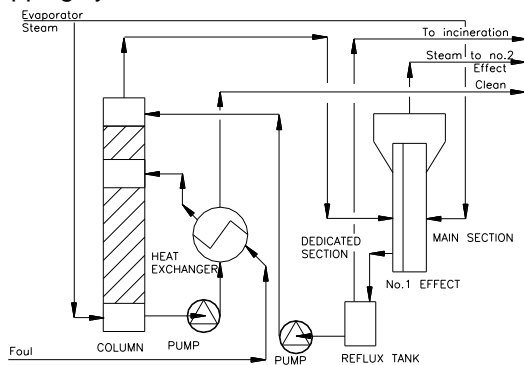Figure 7 is an illustration of a partially integrated stripping system.

Figure 7. *Partially Integrated Column*

COLUMN OPERATION

Stripping columns are generally easy to operate although control schemes for strippers integrated into evaporators can be complex due to their interdependence on evaporator operation. Some problems in column operation are as follows:

Foaming

Liquor in the foul condensate can cause the condensate to foam when air or steam is blown through it. This results in a flooded column where the condensate is carried out the top of the column and steam or air flow is stopped.

This problem is handled by measuring the conductivity of the foul condensate. A high conductivity indicates the presence of liquor and the condensate can be dumped before it gets to the column.

This problem will show up as loss of steam flow to the stripper, or high level in the reflux tank.

At worst, the foam will carry through the stripper off gas (SOG) system and into the incineration point, where it may extinguish the flame, or cause other damage.

Unstable Operation

In steam strippers, where steam use is controlled and based on condensate flow, every change in flow upsets the system for several minutes. In a continuous change situation, such as if the condensate feed flow is based on level control of a foul condensate storage tank, the system remains unstable. Therefore, flow changes should be made on a stepwise basis and made as seldom as possible. In the case of an integrated column, the evaporators used should be run as smoothly as possible.

If a mill has more than one set of evaporators, the set with the stripper should carry a constant base load while the other set takes up the production rate changes. Unstable operation can also cause problems if the stripper gas is burned in a kiln or an incinerator. Rapid changes in MeOH load can upset the heat balance in the kiln or incinerator.

Unstable operation will result in low stripping efficiency.

Steam Collapse

Once the column is started up, it is full of steam. If enough cold condensate enters the column, it will condense the steam where it enters the column, causing an almost instantaneous high vacuum in the top of the column.

The hot condensate in the bottom of the column will boil rapidly, almost exploding. This sudden upward rush will buckle trays, pop them out of their hold down clips, or carry packing out of the column.

Such a situation can happen on a start-up, when there is insufficient hot condensate in the bottom of the column to preheat the foul condensate. Great care must be taken to avoid such situations. Start-ups should be done very slowly.

Loss of trays results in loss of stripping efficiency.

Control of Contaminant Removal

Condensing in the reflux condenser must be controlled to maximise contaminant removal while minimising steam loss. At this point in the process, the system is a very complex, two-phase, multi-component system, mainly made up of water, methanol, reduced sulfur gases and turpentine, but with several other compounds such as ethanol and acetone in lesser quantities.

Good control depends on a combination of pressure and temperature control in the reflux condenser. See **REFLUX CONTROL** below.

Fiber

The foul condensates tend to contain pulp fibers and these fibers can plug packed columns and heat exchangers, especially plate-type heat exchangers. Fortunately, valve tray columns are self-cleaning.

The handling of fiber can be done in two ways. The first is to install a good fiber filter before the heat exchanger. The second is to design the system to pass the fiber through, using valve trays and heat exchangers with wide gaps or large diameter tubes.

This problem normally shows up as loss of flow through the heat exchangers, especially plate type heat exchangers.

Plugging of Heat Exchangers

Several mills have experienced a scale build-up on the stripped condensate side of the heat exchanger. The reason for this is still not clear, and the scale is very difficult to remove. For this reason, the stripped condensate should go through the tube side of the heat exchanger, to facilitate mechanical cleaning.

Attempts to chemically remove the scale have been tried, but with mixed success. Chemical cleaning should be done before the tubes get too badly scaled.

This problem usually shows up as loss of flow of the stripper bottoms, or high level in the bottom of the stripper.

Turpentine in Storage Tank

As there is turpentine in the condensates, there is a tendency for the turpentine to decant in the storage tank, and collect on top of the condensates. If this happens, and the storage tank is pulled down, it is possible to send a slug of turpentine to the stripper.

The turpentine will easily strip, and the turpentine will go through the SOG system, and cause problems at the incineration point, usually a high temperature trip.

There are several means to avoid the turpentine build up in the storage tank. The first is to send the turpentine decanter underflow, which can be rich in turpentine, directly to the suction of the stripper feed pump. The second method is to make sure there is agitation in the tank, to prevent the turpentine decanting. This can be done by making the incoming condensate lines tangential, recirculating feed condensate back to the tank, or by adding an internal agitator.

Skimming the turpentine can also be done. This can either be done periodically, returning the turpentine to the turpentine recovery system, or by continuously skimming the turpentine into the stripper feed condensate.

REFLUX CONTROL

As mentioned above, good control of the reflux cycle is required to operate the stripper efficiently, both with respect to contaminant removal and heat recovery.

For any given operating pressure, and any desired stripper off gas (SOG) concentration, there is fixed equilibrium temperature. Operating at the proper equilibrium temperature and pressure is necessary in order to control the overhead composition.

Further, operating at the proper equilibrium conditions will ensure removal of the turpenes and red oils with the SOG, where they can be burned. If the reflux condensate is allowed to sub cool, the

red oils will separate out, and build up in the reflux cycle until they give control problems.

The concentration of methanol in the SOG is a compromise between stripping efficiency and heat recovery. At higher methanol concentrations, heat recovery improves, but stripping efficiency declines. At lower methanol concentrations, stripping efficiency improves, but heat recovery declines. The generally accepted optimum methanol concentration in the overheads is 50% by weight.

In a non-integrated stripper, it is possible to control both the pressure and the temperature. Two methods of doing this are shown in Figures 8A and 8B.

With an integrated stripper, the evaporator operation will fix the stripping temperature. Thus it is necessary to control the operating pressure based on this temperature.

Temperature control is done by controlling the cooling water flow to the reflux condenser. Pressure control is done by controlling the back pressure on the SOG line.

In the scheme shown in Figure 8A, the temperature of the reflux condensate is measured rather than the gas, which gives faster response to temperature changes. This assumes that the condensate is not sub-cooled, and is at the equilibrium temperature. The condenser is mounted horizontally in order to minimize sub-cooling of the condensate. This scheme works well at design conditions, but sub-cooling tends to occur at reduced operating rates.
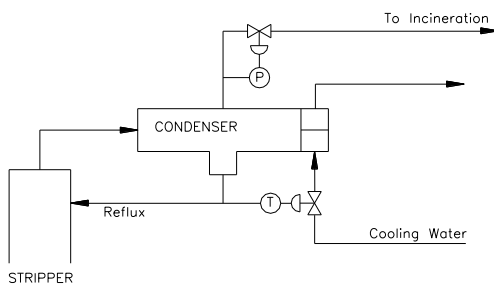

Figure 8A. *Reflux Control*

In the scheme shown in figure 8B, gas temperature is measured directly. Vapor from the reflux condenser is bubbled through the condensate in the reflux tank, which ensures that

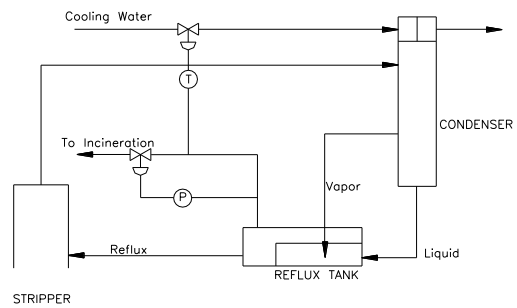liquid and gas phases are in equilibrium. This gives better control, but at a capital cost penalty.

Figure 8B. *Reflux Control*

TRANSPORT AND DISPOSAL OF CONTAMINANTS

Once the contaminants have been stripped out of the condensate and removed from the system, they must be disposed of. The most common way to do this is to carry them in gaseous form and burn them directly in a kiln, boiler or separate incinerator. The system for transport is almost identical to a concentrated or, low volume, high concentration (LVHC) non-condensable gas (NCG) system. See Figure 9.
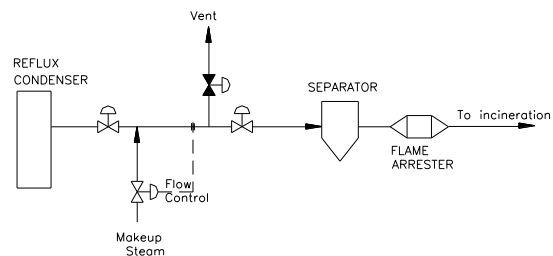

Figure 9. *Stripper Off Gas System*

The major difference with a concentrated NCG system is that the stripper gas system requires makeup steam to ensure purging of the entire system on start-up and to ensure a minimum velocity in the entire line at all times. This is done by measuring the line velocity near the incineration point and adding makeup steam, as necessary, near the pressure control valve at the stripper. The stripper gas system should be operating, with SOG going to incineration, before any foul condensate is sent to the stripper.

The advantages of burning stripper overheads are low cost, simple operation, and recovery of the high fuel value of the contaminants.

The major disadvantage is that if this stream is ever vented, it will create a severe odor problem in the local area very quickly.

It is also possible to collect the contaminants as a liquid by use of an extra condenser. This allows for storage of the contaminants as a liquid, which can be used for fuel or be further refined for recovery of the chemicals.

In the past, the liquid MeOH so collected fell under Resource Conservation and Recovery Act (RCRA) rules classifying it as a hazardous waste, making this form of collection virtually illegal. The Cluster Rule reclassifies this liquid methanol as a "clean fuel", and thus allow it to be collected and stored as a liquid.

In most cases, the SOG will be further rectified to increase the methanol concentration to 85 to 90% by weight.

PROPER OPERATING PROCEDURES

The following procedures have been recently developed to reduce the possibility of steam collapse, and to eliminate venting of SOG during start-up and shutdown.

The stripper should be started up with steam. Once the stripper is fully heated and all air purged out of the system by cracking open the back pressure control valve, feeding of condensate can begin. At a minimum steam flow of about 20% of design, start with a condensate flow of about 10% of design.

After five minutes, increase condensate flow to 20% of design. Continue to increase both condensate and steam flow in 10% increments every five minutes until the full operating rate is achieved.

The slow start-up will prevent damage to the trays due to steam collapse, as well as give the incineration point time to adjust to the changing fuel load from the methanol in the SOG.

As mentioned before, any changes in operating rate should be made in small increments (maximum 10%) and as seldom as possible.

For planned shutdowns, condensate and steam flow should be reduced slowly, until 20% of design is reached. At this point stop the condensate flow, but leave the steam flow on.

The SOG should continue to be sent to incineration until the back-pressure control valve goes closed. At this point steam flow to the stripper can be stopped, and the SOG system (which now contains no pollutants), can be shut down.

In the emergency shutdown situation, such as when the fire goes out at the kiln or incinerator, it is necessary to vent the gases coming off the column.

To virtually eliminate this venting, condensate flow to the column should be stopped immediately and at the same time the pressure control valve at the column should be closed. However, steam flow should remain unchanged.

This will keep the system in thermal balance, which is especially important if integrated into the evaporator. It will also speed up the restart of the system. As before, on the restart, the condensate flow must be brought on slowly.

CONCLUSION

The Cluster Rule requires collection and treatment of foul condensates to reduce Kraft Pulp Mill pollution. The stripping of foul condensates is a good in-plant method of doing this. BOD, toxicity and odor can be reduced by stripping. In most cases, the pollutants can be converted to a usable fuel, giving an economic return on investment.

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CONDENSATE SEGREGATION

Foul condensate stripping is energy intensive when BOD (biological oxygen demand) removal is required; for high efficiency removal, the steam usage is 20% by weight of the foul condensate to be stripped. For example, a 1000 lpm stripper operated at high efficiency for BOD stripping will use about 12,000 kg/h. Reducing the steam consumption will reduce stripping efficiency.

Methanol is typically used as a surrogate for BOD as it typically makes up a very large fraction (80 to 90%) of the BOD in foul condensate. At 20% steaming rates, methanol removal is greater than 90% and TRS removal is over 99%.

Contaminated condensates are generated in a number of locations in the mill. Two of the major areas are the digester area and the multiple effect evaporator systems. If the mill were to strip all of the contaminated condensate generated in these two locations, the system would be prohibitive from both an equipment and operation cost perspective.

Principles of Condensate Segregation

In order to minimize the amount of condensate that needs to be stripped, condensing equipment is typically partitioned into first and second condensing stages. The result is the formation of two types of condensates. The first type, from the first stage, is a "contaminated" condensate that contains some methanol and very little TRS. The second type of condensate from the second stage, "foul" condensate, is highly contaminated in both methanol and TRS and must be treated by stripping. The process which separates these two types of condensate is called condensate segregation.

The main contaminants, methanol and TRS, have a much higher volatility than water. If a water vapour stream containing these components is allowed to condense in series on two distinct surfaces, a larger percent of the more volatile components will carry on to the second surface. The technical term for this phenomenon is differential condensation.

The amount of separation is a function of the percent of the vapour that is condensed on the second surface. For example, referring to Figure 1, if 5% is condensed on the second surface, then of the inlet methanol in the vapour, approximately 65% will be carried to the second surface. If the separation is increased to 15% blow through to the second surface, the percent of methanol carried through will be approximately 80%. In this way a large fraction of the methanol can be captured in a relatively small stream.

Because the TRS components are much more volatile than methanol, the amount of separation will be significantly higher. At the 5 and 15% condensed on the secondary surface, depending on the composition of the TRS mixture, about 95 and 99% of the TRS will be contained in the foul condensate portion, respectively.

Separation can also occur when part of the liquid is flashed. For example, referring to Figure 1, if 5% of the liquid is vapourized, then of the inlet methanol in the liquid, approximately 30% will also be vapourized. If the flash is increased to 15% of the liquid, the percent of methanol carried in the vapour will be approximately 55%. The technical term for this phenomenon is continuous flash distillation.

The theoretical amount of methanol separated is based on a pure methanol - water system. In practice, because Kraft mill condensates are multi-component in nature, methanol separation efficiencies may be slightly reduced.

Theoretical Methanol Recovery
as a function of material vapourized / not condensed in a pure methanol water system
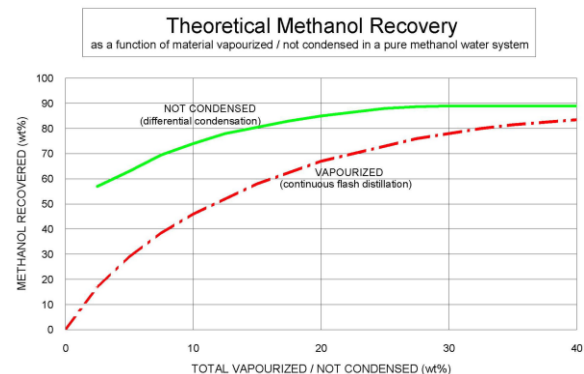
Evaporator Condensate Segregation

It is well documented that a large fraction of the TRS and methanol is flashed off in the first two stages of weak black liquor evaporation. For example, in the first liquor flash of a typical evaporator plant, about 15% of the total liquid is flashed off; the flash vapour will contain about 60% of the total methanol that was in the black liquor. Of the remaining 40% methanol in the

black liquor, 60% of this (i.e. 60% of 40% or 25% of the initial total) will be removed in the second liquor flash; therefore, 60% plus 25% or 85% of the initial methanol in the black liquor will be contained in the condensate from the first two liquor flashes.

The condensing vapour from the first two liquor flashes is typically segregated. This means these vessels are partitioned into first and second condensing stages typically containing 85% and 15% of the heat transfer surface, respectively. To continue our example, about 80% of the methanol from the first liquor flash (containing 60% of the methanol) will be recovered in the foul condensate fraction, i.e about 48% of the total methanol. As well, 80% of the methanol from the second liquor flash containing 25% of the methanol will be recovered in the foul condensate fraction, i.e. about 20%. Therefore, for this segregation system collecting 15% of the condensate from the first two liquor flashes, about 48% plus 20%, or 68% of the methanol contained in the black liquor can be captured in a very small foul condensate stream.

To apply the theory behind condensate segregation, Table 1 lists condensate segregation design features and equipment included for a typical new installation and for a retrofit of an older evaporator set.

Table 1: Evaporator Condensate Segregation Equipment

Equipment	New System	Retrofit Existing System
Weak liquor feed	No split feeding of liquor, all liquor fed to penultimate effect	No split feeding of liquor, all liquor fed to penultimate effect
Last effect	Minimum last 15% of condensing surface segregated for foul condensate	Add external liquor heater, size limited to about 5% condensing
Surface condenser	Minimum last 15% of condensing surface segregated for foul condensate	Add secondary surface condenser in series after existing primary surface condenser; size for minimum 15% of vapour
NCG venting	Last two or more heater bodies vent to foul side of surface condenser	Last two or more heater bodies vent to secondary surface condenser
Vacuum system	Two stage with indirect intercondenser and aftercondenser	Two stage with indirect intercondenser and aftercondenser
Condensate flash tanks	Segregated flash areas inside effects for combined (process) and contaminated condensates for polishing	Add flash tanks on combined (process) and contaminated condensates for polishing

Digester Condensate Segregation

The prin
ciples of condensate segregation can be applied by having a primary flash steam condenser perform 85% of the heat duty and using a secondary condenser to condense about 15% of the flash vapours. After segregation, only the foul condensates from the secondary condenser should be stripped.

The benefits of segregating the digester condensates include:

(a)   Reduced foul condensate loading to the stripper.

(b)   Reduced foul condensate loading for turpentine decanting (as turpentine is also very volatile and 99+% will be contained in the secondary condensate).

(c)   Improved heat recovery, i.e. instead of heating cold mill water, 105°F warm water can be heated to 185 to 190°F in the primary condenser.

Kraft Mill Condensates

In general, there are three types of Kraft mill condensates - combined (or process), contaminated, and foul (see Table 2).

TABLE 2: Types of Kraft Mill Condensates

	Combined (Process) Condensates	Contaminated Condensates	Foul Condensates
Typical TRS concentrations	40 ppm	150 ppm	600 ppm
Typical methanol concentrations	100 ppm	500 ppm	3000 ppm
Typical volumes	8000 lpm	4000 lpm	1500 lpm

Combined condensates are the cleanest and the largest volume of the three. Combined condensates are often reused at brown stock washing and/or at recausticizing without any further treatment. Typical combined condensates include:

(a)   The front end of the evaporators, i.e. the 2nd effect through to the penultimate effect of the evaporator plant.

(b) Stripped condensate. The cleaned condensate from a foul condensate stripping system. Requirements: minimum 20% stripping steam.

(c) Primary flash steam condenser. The condensates from the first condenser of a two stage digester condensing system. Requirements: primary condenser must be operated at a vent temperature of no less than 210°F; in this case the mill would have a single condenser and send all of the condensate to stripping.

Contaminated condensates are in between combined and foul condensates in contaminant concentration. These condensates are generally too odourous for reuse in the mill and are usually used for level controlled makeup to the stripper feed tank. Typical contaminated condensates include:

(a) the condensates from the primary split of the last effect of the evaporators. Requirements: the liquor feed effect is to penultimate effect; up to 85% is condensed in the primary surface.

(b) The condensates from the primary split of the surface condenser. Requirements: up to 85% of the vapour is condensed in the primary surface.

Foul condensates are the most odourous and BOD concentrated condensates found in the Kraft mill. Sending to secondary treatment without in-plant treatment such as steam stripping will result in higher odour and BOD loading at the lagoons. Typical foul condensates include those from the back end of the evaporator including segregated portions from the first two (and sometimes three) liquor flashes:

(a) The condensates from the secondary split of the last effect of the evaporator. Requirements: 15 to 25% of the vapour is condensed in the secondary surface.

(b) If the last effect is not segregated, then the condensates from an external liquor heater off the last evaporator effect. This is not as effective as segregating the last effect surface area as listed in (a) above as liquor heating duty limits the vapour condensed to about 5%.

(c) The condensates from the secondary split of the evaporator surface condenser or a secondary surface condenser. Requirements: 15 to 25% of the vapour is condensed.

(d) Evaporator vacuum system. Condensates from the two stage vacuum system. Requirements: indirect precooler, intercondenser, and aftercondenser.

(e) Secondary flash steam turpentine condenser. The condensates from the second condenser of a two stage condensing system. The condensates are first sent to turpentine decanting first. Requirements: primary condenser must be operated at a vent temperature of no less than 210°F.

(f) NCG/SOG line drains. Line drains from the NCG and SOG headers are collected and pumped to the stripper feed tank.

(g) Turpentine storage tank padding water. If a mill collects 300 US gallons of turpentine per day, then the padding water flow will be 0.2 gpm.

METHANOL PURIFICATION PROCESS OVERVIEW

Methanol is produced as a by-product of the Kraft pulping process. A large fraction of this methanol is recovered in the foul condensate steam stripping system. The stripper off gas (SOG) is condensed to produce a crude methanol solution, which is upgraded to minimum 99.85wt% in the methanol purification system (see Figure 1). Methanol purification is based on the unit operation of distillation, including two separate stages. In the first "topping" stage, the compounds more volatile than methanol, such as H_2S and ammonia, are removed in the vapour phase while the methanol, water and other less volatile compounds remain in the bottoms. In the second "rectification" stage, the purified methanol is recovered from near the top of the column while the water and other less volatile compounds are removed in the bottoms.
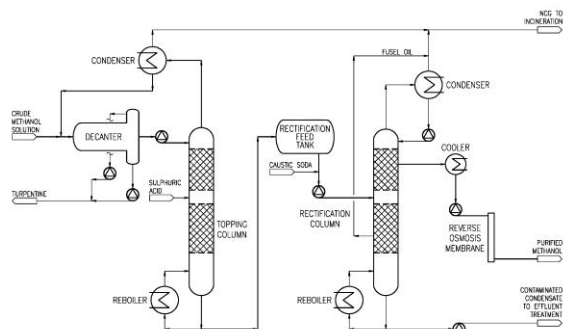

Figure 1: Methanol Purification System Process Flow Diagram

There are numerous methanol purification systems in service around the world and their operation is well understood, but this process had not previously been applied to this feed stream. Recovery of methanol from Kraft pulping condensates has several unique characteristics that inhibit separation by distillation:

➔ Azeotropes of methanol and organic contaminants
➔ Immiscibility of terpenes
➔ Dissociation of hydrogen sulphide and methyl mercaptan
➔ Ammonia reacting to produce ammonium sulphate (fouling)

A.H. Lundberg has developed and patented features to deal with each of these design issues.

Modular Construction

The Methanol Purification System is supplied in modular form (see Figure 2). All equipment, inter-connecting piping, handvalves, instruments, control valves, insulation and access stairways and ladders are supplied pre-assembled on steel skids.

Figure 2: Methanol Purification System Modules

PROCESS DESCRIPTION

The presence of azeotropes between methanol and some organic contaminants require that the SOG generated in the stripping system be no higher than 40wt% methanol to ensure separation of the contaminants in the topping system. Effective distillation requires a consistent feed stream; therefore, the SOG quantity as well as quality must be stable. In some cases, this requirement will necessitate upgrades to the stripping system.

The SOG is condensed and stored as a crude methanol solution. Typically about one hour of retention is recommended; this gives operational flexibility and provides volume to homogenize the feed flow to the methanol purification system.

Topping System

The crude feed solution is composed mainly of methanol and water, but it also contains over 150 different inorganic and organic "impurities" including various aliphatic alcohols and ketones, and terpenes, along with many sulphur and nitrogen compounds. The topping column is

designed to strip out the "low boilers" and noncondensibles, including the odorous total reduced sulphur (TRS) compounds, ammonia, and some ethers, ketones, and aldehydes.

The crude methanol solution is first introduced to the red oils (turpentine) decanter for separation and removal of terpenes. From there it is pumped to the top of the topping column, where it flows down through the packing countercurrent to the stripping steam, thereby driving off the volatile constituents to be removed from the less volatile (methanol, water, etc). Heat is added to the topping column via an integral bayonet type steam reboiler. The overhead vapours from the column are condensed in the topping reflux condenser with the heat recovered into cooling water. The low boilers and noncondensibles from the reflux condenser are vented to the NCG system while the reflux condensate is drained to the decanter.

Contaminants produced during the kraft pulping of wood include the ionizable sulphur compounds, hydrogen sulphide and methyl mercaptan. The removal of these compounds by distillation is directly related to the pH of the liquid phase in the column. For example, at a pH above about 6, hydrogen sulphide begins to dissociate, and at a pH above about 9, this occurs with methyl mercaptan (see Figure 3). In their dissociated form, these compounds do not exert a vapour pressure and therefore cannot be removed by distillation.
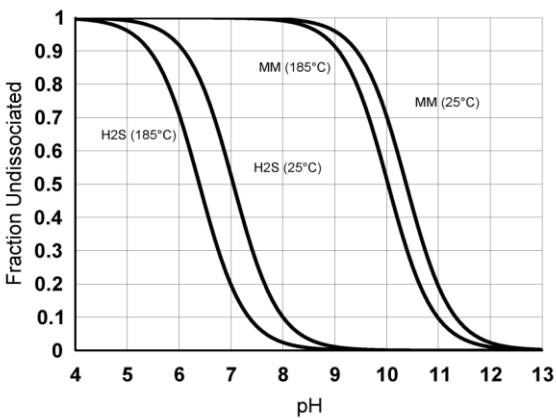

Figure 3: Dissociation of Hydrogen Sulphide and Methyl Mercaptan

The pH of condensed SOG is typically slightly alkaline at about 9 to 10. To ensure that ionizable sulphur compounds are removed, sulphuric acid is added to the topping column. Due to the presence of ammonia, the acid cannot simply be added to the liquid feed to the column as it will react with ammonia producing ammonium sulphate.

Ammonium sulphate is very soluble in water (about 0.7 kg dissolved per kg water at 25°C and 1.0 kg per kg at 100°C), but essentially insoluble in methanol. To ensure that no ammonium sulphate forms, potentially fouling the topping column, the sulphuric acid is added at the mid-point of the column; the top section of the column is therefore used to strip out the highly volatile ammonia before is has a chance to react with the acid.

Sufficient acid will be added to lower the pH to between 5 and 6, thereby releasing the newly undissociated hydrogen sulphide and methyl mercaptan. These are stripped out in the bottom section and then must rise up through the top section of the column. These gases, when reabsorbed, are weak acids and will cause a slight decrease in the pH in the top section of the column, but no ammonium sulphate precipitate will form due to lack of any sulphate ions in solution.

Red Oils Decanting

Terpenes, naturally present in wood, are extracted during kraft pulping, and due to their extremely high relative volatility, will be stripped from stock and liquor streams and collect in foul condensate. Those not decanted in the turpentine recovery system will make their way to the stripping system and subsequently into the SOG. The mixture of terpene compounds is referred to as turpentine, or crude sulphate turpentine, or, when heavily contaminated with TRS compounds, "red oils", due to their distinctive red hue. The terpenes are almost totally immiscible in the methanol solution; therefore a red oils decanter is required. If turpentine is disposed of through incineration, then the red oils can be pumped to the turpentine recovery system. If turpentine is sold, the red oils should be processed separately as their high TRS content will degrade the quality of regular turpentine.

Rectification System

The underflow from the topping column flows by gravity to the rectification feed tank. This tank is sized for one hour of retention; therefore, it provides operational flexibility by separating the topping system and rectification system

processes. The tank also provides volume to homogenize the methanol solution feed flow to rectification.

The methanol solution from the feed tank is pumped to the rectification column, and flows down through the stripping section countercurrent to the stripping steam, thereby driving off the volatile constituent (methanol) to be removed from the less volatile (water, ethanol, etc). This column is designed to separate the water and other "high boilers" into the underflow, and methanol vapour into the overhead vapour flow. Heat is added to the rectification column via an integral bayonet type steam reboiler.

"Intermediate boilers," those with boiling points between methanol and water, referred to as "fusel oils," are drawn off from the bottoms column below the methanol solution introduction point. The fusel oils include some higher alcohols (primarily ethanol) and higher ketones (primarily methyl ethyl ketone). They are combined with the underflow from the column, but can in future be recovered separately if desired. Typically a fusel oil flow sacrificing about 2 to 3% of the methanol must be bled off to ensure that the methanol product remains free of ethanol contamination. The contaminated condensate from the rectification column is pumped away to effluent treatment.

The vapour from the top of the stripping section passes up to the rectification section. Vapour from the top of the column is condensed in the rectification reflux condenser, with low boilers and noncondensables (not removed in the topping column) vented to the NCG system. The heat introduced by the reboiler steam is recovered into cooling water in the rectification reflux condenser. The reflux condensate is pumped back to the rectification column.
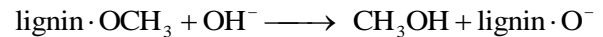
Methanol Product

The methanol product is drawn off slightly below the top of the column. The methanol is withdrawn in sufficient quantity to maintain the temperature (and therefore methanol concentration) profile in the column. The methanol is cooled and then pumped through a reverse osmosis (RO) membrane for final polishing. The 99.85wt% methanol product is then directed to storage. If necessary, the methanol product can also be recycled back to the stripper feed tank, crude

methanol tank, rectification feed tank, or disposed of through incineration in a boiler or the lime kiln.

METHANOL RECOVERY AND USAGE

Methanol Formation

Methanol is formed as a by-product of the kraft pulping process; in the digester, the hydroxyl ion reacts with a lignin methoxyl group:

$$\text{lignin} \cdot OCH_3 + OH^- \longrightarrow CH_3OH + \text{lignin} \cdot O^-$$

The amount of methanol produced is dependent on:

➤ Wood species: in general lignin methoxyl groups are more numerous in hardwoods than softwoods therefore more methanol is formed.
➤ Hydroxyl concentration: higher alkali charge will produce more methanol.
➤ Temperature: higher cooking temperatures will produce more methanol.
➤ Time: longer cooking times will produce more methanol.

Some methanol is also formed from the acid-catalyzed methanol elimination from hemicellulose, while naturally occurring methanol is freed from the biomass at the start of pulping.

Estimates are provided in Table 1 for methanol formation in the digester when producing bleachable grade Kraft pulp from various softwoods and hardwoods.

Table 1: Methanol Formation in Kraft Pulping

Wood Species	Methanol Formation (kg/ADT Pulp)
Western Hemlock	6.6
Douglas Fir	7.5
White Spruce	8.2
Southern Pine	8.4
Aspen	8.6
Birch	9.9
Maple	10.2
Oak	11.5

Bass	11.8
Sweetgum	13.5

Methanol Capture

In a continuous mill, the methanol leaves the digester with the extraction liquor or with the brown stock. Methanol is relatively volatile compared to water; therefore, a large fraction will tend to flash-off in the extraction liquor flash tanks and collect in the flash steam condenser foul condensate. In a batch mill, a large fraction of the methanol will leave the digester with the relief steam and collect up in the relief steam condenser foul condensate. Additional methanol is captured in the foul condensate from the blow heat recovery system.

Some methanol will be carried away by the digester Concentrated Noncondensible Gas (CNCG) collection system and some will be lost to the Dilute NonCondensible Gas (DNCG) system during brown stock washing. The methanol that is captured in the washing filtrate will eventually end up in the weak black liquor feed to the evaporators. Depending on the level of condensate segregation, anywhere from 50 to 90% of the methanol in the weak liquor can be captured in the evaporator foul condensate, with the remainder lost to the combined condensate and the CNCG vent.

Up to 80% of the methanol formed in the digester will end up in the foul condensate. In a well operated stripping system, up to 95% of the methanol will be removed from the foul condensate and captured in the SOG, with up to 90% of this recovered as purified methanol. Overall, up to about 70% of the methanol formed in the digester can be recovered as purified methanol.

Methanol Product

Methanol at a purity level of 99.85wt% can be worth over five times as much as a traded commodity than in crude form as a combustion fuel, displacing light fuel oil or natural gas. Typically about 30 to 40% of the methanol produced at a bleached Kraft mill can be used internally for production of chlorine dioxide (ClO_2), with the balance for external sale.