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"The Effects of Steam Stripping Contaminated Kraft Condensates"

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**"THE EFFECTS OF STEAM STRIPPING
CONTAMINATED KRAFT CONDENSATES"**

by

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A Thesis submitted to the
Faculty of the Department of Paper Science
and Engineering in partial fulfillment
of the Degree of
Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

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OBJECTIVE

The objective of this thesis is the analysis of the effects of steam stripping contaminated Kraft condensates. This will be accomplished by the systematic distillation of Kraft effluent streams and the subsequent analysis of the products by gas chromatography. The analysis will concentrate on the removal of odorous sulfur-containing products. This study will center on the recovery area of the process with samples coming from two multiple effect evaporator systems and a concentrator. Waste heat evaporator data will also be shown.

In addition, actual mill data will be used to show the relative importance of each stream, and the BOD contribution of each to total BOD output. Included will be cost, and process water considerations that will add to the attractiveness of the stripping installation.

ABSTRACT

The effects of steam stripping contaminated Kraft condensates were evaluated in relation to the removal of odorous sulfur-containing compounds. The investigation was carried out in a packed distillation column. The mill streams investigated were multiple effect evaporator condensates, waste heat evaporator condensates, and concentrator condensates.

Measured volumes of distillate were removed and analyzed for chemical oxygen demand by oxidation, and for component make-up by gas chromatography.

This study indicates that the use of steam stripping not only reduces the amount of sulfur-containing compounds, but reduces mill water requirements and the BOD load placed on effluent treatment facilities.

BACKGROUND

Studies on the possibility of steam stripping Kraft effluents were begun in 1956 by Robert Whittaker.¹¹ Since that time only three papers have been published directly pertaining to the SEKOR process.^{11, 15, 16}

There is at present only one commercial installation in operation in Sweden. Recently the government has issued a grant to the Weyerhäuser Company, Springfield, Oregon, division for the installation of a full-scale column.

The goals of the SEKOR process are: 1) the elimination of Kraft odor by steam distillation, 2) the production of significant amounts of hot, reusable process water, and 3) the recovery of malodorous sulfur, terpene, and alcohol compounds for possible commercial sale.

The primary organic constituents of contaminated mill condensates are α -pinene, limonene, and α -terpineol. Figure 1 shows their solubility in water as a function of temperature. From this graph it can readily be seen that at temperatures approximating the boiling point of water, the combined solubility of these oils is less than .25 g/l. Near 100°C the solubilities of sulfur-containing organics are also small. The compounds of interest in the pulping process are: hydrogen sulfide, H_2S ; methyl mercaptin, CH_3SH ; dimethyl sulfide, $(CH_3)_2S$; and dimethyl disulfide, $(CH_3)_2S_2$.

By fractionally distilling contaminated mill effluent streams, notably evaporator and blow gas condensates, the virtual elimination of malodorous sulfur emissions from both stacks and settling ponds can be attained. Due to low solubility, these terpene oils and sulfur compounds will collect at the head of the stripping column. By passing this distillate through a phase separator any carry-over water may be removed. The resultant liquid is a heavy, terpene-sulfur rich oil.

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Because the distillation operates at temperatures below the boiling point of water, low pressure steam is a sufficient heat source. An optimum feed-to-steam ratio has been reported at 50. Other design and cost parameters will be discussed later.

There are two basic questions that arise: First, what will be gained? and second, how much will it cost?

This thesis will indicate that virtually complete elimination of sulfur-containing compounds from the recovery process is possible. The subsequent SEKOR oils produced may also have a commercial value; if not, they may be used as fuel in a lime kiln or power boiler. Two major sources of sulfur odor have thus been minimized.

The first is from retention ponds where microbial attack on sulfur compounds produces hydrogen sulfide. Second, removal of these oils also reduces the load on the effluent treatment system and correspondingly the total discharge of BOD to the waterways. It will be shown that stripping the discharge from the multiple effect evaporators can produce at least a 10% decrease in total BOD discharge.

In many Kraft mills, especially those located near metropolitan areas, the future expansion and perhaps the very existence depends on the ability to maintain and even reduce pollution levels. With tightening controls and the expense of secondary treatment, steam stripping may be part of the answer.

The cost figures for steam stripping all digester and evaporator condensates have been calculated for a 400 TPD mill on a five year write-off. The total capital with 15% contingency is \$84,000. The cost per ton of production, including maintenance, is \$.32 for the first five years, and \$.21 thereafter.¹⁵

Fig. 1 Solubility of Terpenes

NATIONAL
12-862 125
MADE IN U.S.A.

INC. IN

3/2

.75

.50

.25

0

20 Squares to the Inch

20

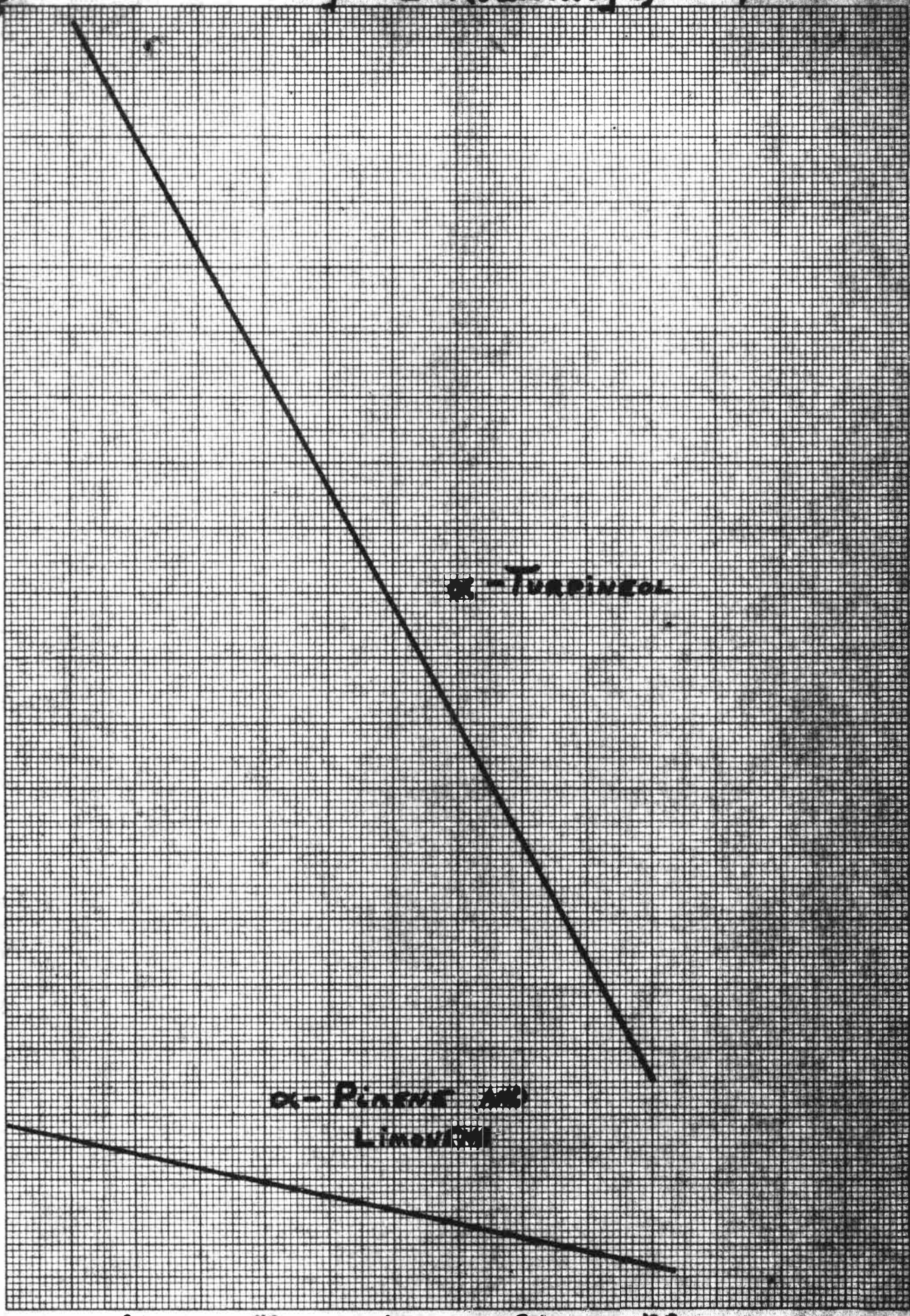
40

60

80

100

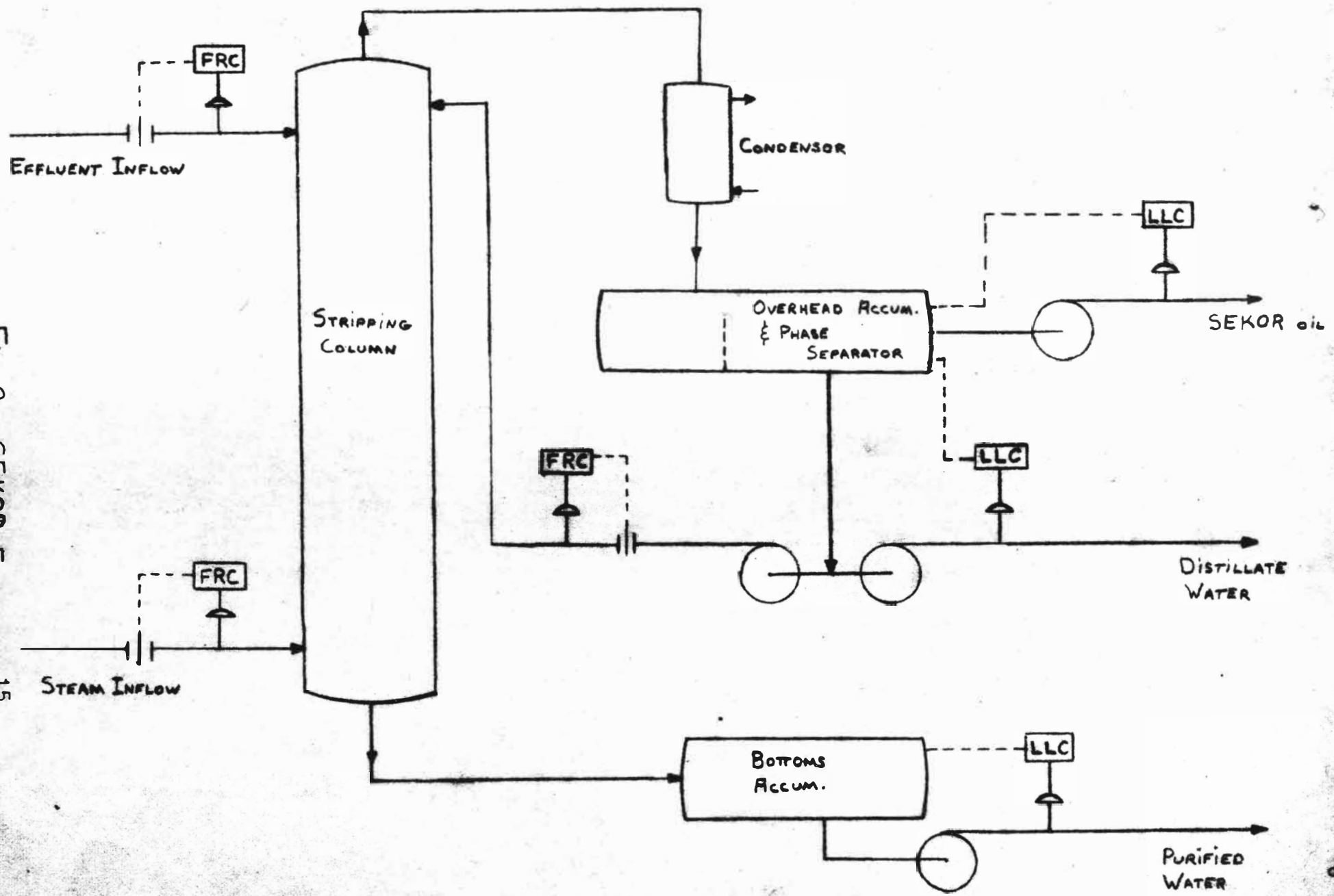
TEMPERATURE IN °C



α -TURPENEOL

α -PINENE
Linoleum

Fig. 2 SEKOR FLOWSHEET 15



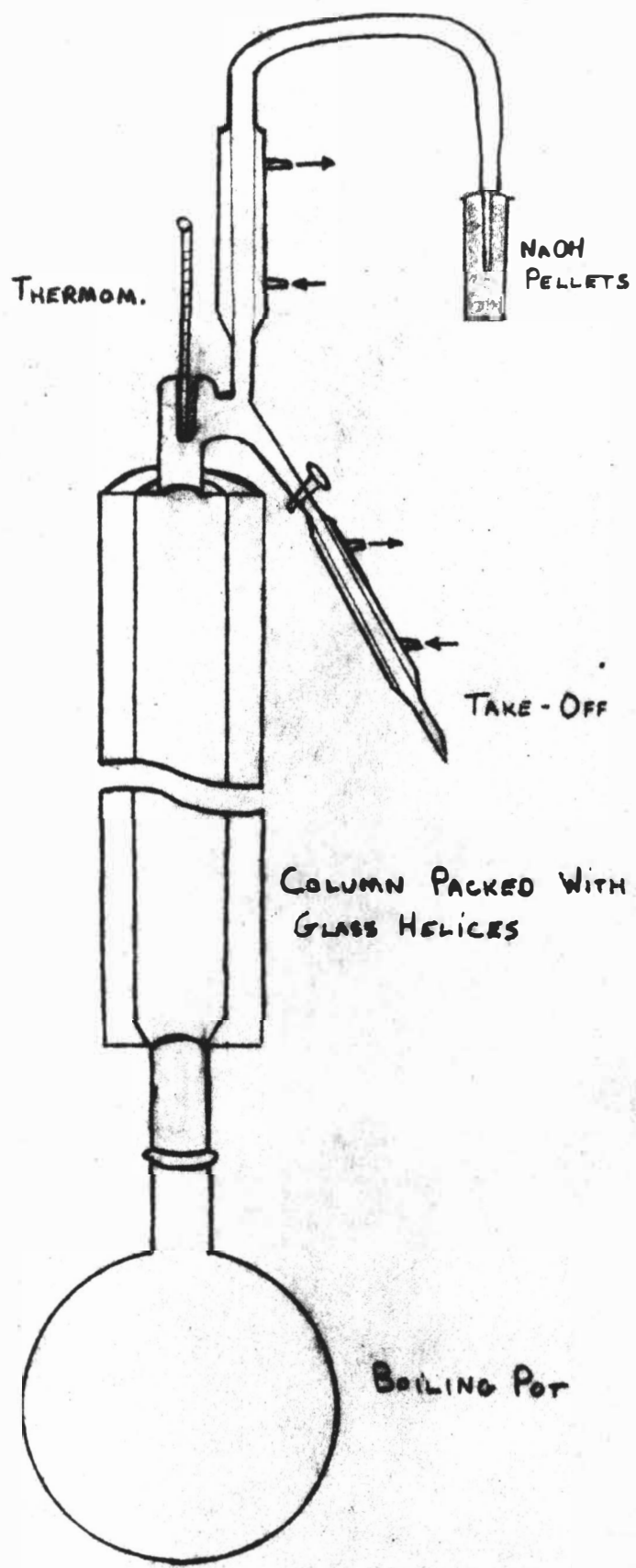


FIG. 3 LAB DISTILLATION COLUMN

PROCEDURAL JUSTIFICATION

The SEKOR process involves the distillation of the contaminated effluent. The parameters involved include effluent feed rate, steam feed rate, and out-flow rate. The actual column system designed by Whittaker¹¹ is pictured in Figure 2. The reproduction of the effects involved would require either a similar pilot column or the use of a static analog of this process.

The latter method was employed. Each characteristic of the actual SEKOR column was copied by a theoretical or physical model. For instance, live steam is injected into the column causing dilution of the condensate. The optimum feed-to-steam ratio for a column removing 99% of the dimethyl disulfide is 50.¹⁵ Combining these two facts, it was obvious that if the original samples were diluted by 1:50, a simple fractional distillation could mimic the effects of the SEKOR column.

The SEKOR column, designed for 99% removal of dimethyl disulfide, used a series of thirteen condensing plates. A benzene-toluene distillation was run on the simple fractional distillation column. By using refractive index measurements and vapor pressure data, it was determined that the lab column had fourteen theoretical plates.

Thus all of the parameters of the two columns were equated. A fractional distillation column packed with glass helices, thirteen HETP (theoretical plates), and with properly diluted samples was used for the experimental distillation.

One feature was added to the apparatus which was not justified by the actual column. Due to the extremely low boiling points of hydrogen sulfide and methyl mercaptan, it was feared that an ordinary condensing column would not trap these vapors. After considering several alternatives, a hose was attached to the top of the con-

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densing column and submerged in sodium hydroxide pellets. This served as a scrubber and eliminated the odor that would have been caused by these noncondensables.

The calculated volume of SEKOR oil and water at the take-off was 10% of the inflow volume. It was decided to take only 1% of the inflow volume as a sample. By the nature of the distillation column, a certain amount of oil would remain in the column and therefore even by withdrawing the full 10%, a certain amount of oil would be uncollectible. The optimum results could still be attained by knowing the water and oil concentration before and after stripping.

To relate the results to daily mill operation, chemical oxygen demand, COD, was chosen over the traditional five-day BOD test. The BOD test depends upon microbial attack and digestion of organic compounds in the effluent. At the end of five days, significant amounts of oxygen demand still remain in the test specimen. Compounds in the sample, such as phenols, may be poisonous to the microbes. Only microorganisms from the family Pseudomonis are capable of phenolic digestion. Thus the presence of these phenols could give deceptively low results. In the COD test, both biodegradable and chemodegradable substances affect the results.

In contrast to the BOD, COD tests employ a dichromate, acid oxidation. With the addition of a silver sulfate catalyst, the only organics which will not be oxidized are the aromatics. This method is also superior to permanganate oxidation in reproductivity, stability with regard to ammonia oxidation, and ease of manipulation.

Between the test results from BOD and COD, there exists a distinct factorial relationship for each effluent tested. BOD usually ranges from 0.5 to 0.7 of the corresponding COD value.¹ Due to the magnitude of errors involved in the repeated dilutions that would be required, for the BOD, and arbitrary value of 0.6 was chosen for

the relationship.

Gas chromatography was selected for the analysis of the effluents before and after stripping. By this technique, quantitative information was available as to the effectiveness of stripping. Information of this nature was essential if comparison of effluent streams was to be made.

For this analysis a ten foot, $\frac{1}{4}$ inch diameter, 5% Carbowax column was used. The use of this column allows separation of alcohols, aldehydes, aromatics, ketones, sulfur compounds, and terpenes. All of the above were suspected contents of the effluent streams.

PROCEDURE

Two gallon samples of contaminated condensate were obtained from four different pulp mill effluent streams. The samples were shipped in plastic containers from the Weyerhaeuser Company, Springfield, Oregon, division. The samples were from the waste heat evaporator, #1 and #2 Recovery evaporators, and #2 Recovery concentrator. During transit the samples were kept refrigerated.

One liter aliquots of the effluents were diluted to 1020 ml in accordance with the 1:50 dilution by steam. Each aliquot was then fractionally distilled in the aforementioned column. (See Figure 3.) The reflux ratio was chosen as 10:1; that is, ten drops of distillate were returning to the column for every one drop removed at the take-off valve. One per cent of the initial volume, or 10.2 ml, were removed as what will be referred to as secondary condensate.

An essential feature of any distillation is the establishing of an equilibrium in the column. At least forty minutes of refluxing was allowed before any secondary condensate was removed.

After the secondary condensate had been removed, but before the column had a chance to cool, a 100 ml sample was removed from the distillation flask. This sample will be referred to as underflow.

It is essential that all of these samples--inflow, underflow, and secondary--be refrigerated. This is essential to reduce the effects of both aerobic and anaerobic decomposition. Even when stored in a refrigerator, a cloudy white scum will form on the sample surface.

The samples removed at the take-off were slightly emulsified. Rather than try to break this emulsion and decant the SEKOR oils, it was decided to completely emulsify the samples and run the analytical tests on the com-

posite of water and oil. The samples in volumetric flasks were subjected to ultrasonic vibrations for three minutes each. Aliquots were immediately withdrawn for COD testing.

The standard dichromate acid COD test was run on each of the samples.⁵ Due to the dilution errors involved in the test, results were reported to only two significant figures.

The final portion of the testing involved analysis by gas chromatography. The analysis was done on a ten foot, $\frac{1}{4}$ inch diameter, 5% Carbowax-20 M column. To eliminate sampling problems, only the inflow and outflow portions of each sample were tested. The actual analysis proceeded in two phases.

Phase I involved implanting the species in the column. This was accomplished by the following set of conditions:

Temp. Limits	75-225° C
Recycle	
Rate of Temp. Change	10° C/min.
Upper Limit Int.	20 min.
I. Port Temp.	270° C
Flame Det. Temp.	170° C
Chart Speed	.25 in./min.
Range	10
Carrier Flow (He)	125 cc/min.
Sample Size	10 ml

Phase II involved pushing the components through the column. This was affected by increasing the temperature. The following conditions were changed:

Temp. Limit	400-490° C
Rate of Temp. Change	60° C/min.
Hold	

The sample after injection is held at the head of the column until the characteristic temperatures of the components are reached. The components then proceed through the column. By slowly increasing the temperature, separation is achieved. By lowering the temperature, greater separation is achieved. Once separation has occurred in Phase I, the purpose of Phase II is simply

to speed the components through the column. Although some fractionation efficiency was lost, the reduced time element and adequate reproducibility made the approach advisable. Even using this method of fractionating, each sample required about two hours to pass through the column.

DATA

The effluent samples were obtained from the Springfield, Oregon, division of the Weyerhaeuser Company. Four condensate samples were obtained, including: waste heat evaporator, #1 Recovery multiple effect evaporator, #2 Recovery evaporator, and #2 Recovery concentrator. The mill is a 1300 TPD integrated Kraft board mill utilizing 80% Douglas Fir and 18% Ponderosa Pine.

Table 1 Average COD

	#1 E.C.	#2 E.C.	#2 Conc.	W.H.E.
Inflow (mg/l)	290	310	270	380
Outflow (mg/l)	120	200	110	180
Take-off (mg/l)	850	800	800	100

Table 2 Removal of Sulfur Compounds*

	#1 E.C.	#2 E.C.	#2 Conc.	W.H.E.
hydrogen sulfide	80%	80%	100%	60%
methyl mercaptin	100%	80%	100%	60%
dimethyl sulfide	10%	10%	30%	N.A.*
dimethyl disulfide	100%	100%	100%	100%

*The recorder on the chromatograph developed mechanical problems. The pen would not hold a steady zero point throughout a single run. The resultant graphs have zero points wandering as much as two inches. This eliminated the possibility of quantitative reporting of sulfur concentrations. The figures in Table 2 can therefore represent only approximations obtained from the graphs drawn by the chromatograph.

Table 3 Unknowns Actually Located in Sample

<u>Component</u>	<u>Time Units</u>	<u>B.P. in °C</u>
hydrogen sulfide	.7	-60
methyl mercaptan	4.0	6
dimethyl sulfide	8.0	37
acetone	10.7	56
methanol	11.4	65
ethanol	12.1	79
water	13.5	100
*methyl isobutyl ketone	20.3	108
dimethyl disulfide	22.2	116
α-pinene	23.8	156
limonene	26.0	178
α-terpineol	28.0	220

*Not certain that is the actual compound

DISCUSSION OF RESULTS

The important factor to remember in analyzing these results is that the difference between the inflow and outflow volumes is only 1%. Only 1% of the inflow is the secondary condensate. The design specifications called for 10% of the inflow to be taken off as secondary condensate. The sample analyzed is richer in alcohols and lower weight sulfur compounds.

It may be noted from Table 1 that stripping eliminates hydrogen sulfide in the samples. The stripping also produced high removal efficiencies of methyl mercaptan and dimethyl sulfide. All of these sulfur-containing compounds have boiling points below that of water. Dimethyl disulfide has a boiling point in excess of 100°C. The removal efficiencies were therefore low. The amount of dimethyl disulfide was higher for the concentrator effluent. This is because of the absence of terpene oils in the concentrator stream. This would tend to down-grade the importance of the concentrator in the stripping scheme.

Flow rates and BOD output data were obtained from the Springfield mill. These will give a vivid picture of the importance of each condensate stream in relation to total mill output of BOD.

Average Production		1000 TPD
Average BOD to Ponds		37,800 #/day
Average Treatment Efficiency		92%
#BOD in the Condensate/day:		
#1 E.C.	2040	5.4% of total
#2 E.C.	1860	4.9% of total
#2 Conc.	110	.3% of total
W.H.E.	480	1.3% of total
	<u>4490</u> #/day	<u>11.9%</u> of total BOD

Assuming a 90% efficiency of BOD removal during stripping, the amount of BOD going to the retention ponds will decrease by over 10%. Assuming no increase in pond effi-

ciency, the BOD going to the river will decrease by .8%. Another feature of the decreased pond load will be total water output. With the reuse of the hot process water, the total mill requirement of water will be reduced by three million gallons per day, or 16%.

In addition to the savings in water pollution, and perhaps less tangible, are the savings in air pollution. The removal of 1% of the inflow volume of effluent reduced the average sulfur content of the outflow stream by 75%. This represents a tremendous reduction in sulfur content when all 10% of the inflow volume is removed.

All of the compounds identified in Table 3 are potential odor hazards. If these compounds are sent directly to the effluent treatment system, odor can be the only result.

This thesis does not intend to say that retention pond odors will be eliminated. There will always be some degree of odor associated with the aerobic decomposition in the treatment system. This process will eliminate sulfur emissions characteristic to the Kraft process, and odor from the decomposition of terpene oils.

From the data presented and the chromatographs of the effluent, the relative importance of each condensate stream may be evaluated. The multiple effect evaporators are obviously high in BOD output, amounting to about 5% of the total BOD output. The waste heat evaporator, although low in the total output scheme, is rich in turpentine and sulfur compounds. The concentrator, in contrast, is low in terpenes and sulfur, and would probably not be considered as a steam stripping inflow.

Several other areas of mill condensates would warrant investigation. Among these are blow gas condensates and turpentine decenter underflows. An analysis of each of these flows should be made to determine the amount of oil and sulfur present. The ranking of these flows will aid in the final decision of whether steam stripping is

practical for a given mill situation.

Although the quantitative portion of this thesis may be considered a failure, the results obtained still substantiate one major point. Steam stripping is effective in the reduction of sulfur and turpene portions of mill effluent. Despite these observations, there are several practical considerations which may lower the effectiveness of the process. The steam stripping process will not remove color bodies from the inflow stream. Any black liquor carry-over from the evaporators or the concentrator will not be removed. This material is composed basically of heavy wood sugars and lignin compounds. As was observed in the case of the concentrator inflow, the outflow was nearly the same color. This may limit the acceptability and range of uses for the volumes of process water produced.

The stripping column is designed for a particular set of flow conditions. Increasing the flow rate will, despite increased steam flow, lower column efficiency. The end use of the process water must be flexible enough to allow varying degrees of water purity.

The third problem was an empirical observation made during the distillation. Some of the secondary condensate came out in the form of an emulsion. If an emulsion formed in the condenser or phase separator, stripping efficiency would drop off. Due to the hydrogen bonding and polarity of the terpene oils, the problem could be significant.

Due to the volatile nature of hydrogen sulfide and methyl mercaptin, the non-condensable gasses from the process could not be vented to the atmosphere. The gasses would then have to be passed either into the lime kiln or into a specially designed burner for odor-free operation.

The beneficial effects of steam stripping seem to outweigh potential problems. For the elimination of

Kraft odor, some form of volatile component removal is mandatory. Steam stripping seems to meet both the economic and the easy operational parameters for industry adoption.

SUMMARY

Steam stripping provides an efficient means of Kraft odor removal. Not only has it been shown effective in odor removal, but in lowering the total mill water requirements and BOD output to the waterways. Eleven odor-producing compounds were identified in the effluents studied.

The stripping process also meets the crucial economic considerations essential to the industry today. A 400-ton per day mill can strip evaporator condensates and blow gas condensates at a cost of \$.32 per ton for the first five years, and \$.21 per ton thereafter.¹⁵

As was demonstrated in the example of the Springfield mill, not only can mill water demands be reduced by up to 16%, but total BOD to the effluent ponds can be reduced at least 10%.

Mill effluent streams should be tested, and calculations should be made to determine the gain involved in stripping each stream. Expansion of mill facilities in many areas may depend on the mills' ability to maintain present pollution levels. Although there are several problems involved, the net advantage to the paper maker, both in public relations and in meeting state pollution regulations, will be immeasurable.

Literature Survey

1. Key Words: Alkaline, Black Liquor, Chemical Testing Chromatography, Condensate, Effluent, Machinery, Pollution, SEKOR, Steam Stripping, Stream Pollution

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