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Gary Paul Burns (M.S. thesis)

May 1979

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ENERGY REDUCTION IN PHENOL RECOVERY SYSTEMS

Gary Paul Burns
(M.S. thesis)

May 1979

Lawrence Berkeley Laboratory
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Abstract

A number of processes use liquid-liquid extraction to recover phenol from waste water streams. A set of criteria for the selection of a solvent suitable for phenol recovery was developed as part of a study to improve the energy consumption and/or reduce the complexity of such a phenol recovery process. Methyl isobutyl ketone (MIBK) was identified as being nearly ideal. Mutual solubilities and distribution coefficients were obtained for the system Phenol-Water-MIBK at 30°, 50° and 70°C. In addition, a relatively simple process was developed for phenol recovery that offers significant energy savings. A mathematical model of the steam stripper for recovering MIBK from water was used in the development of the process.
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Introduction and Background

Petroleum refining, petrochemical, and coal-processing plants each produce waste waters containing phenolic compounds in concentrations up to several weight percent. There is considerable economic incentive to recover these dissolved compounds. Additionally, phenolics are toxic and particularly offensive pollutants, not only because of their contribution to the Biological Oxygen Demand (BOD) and their lethal effect on many fish but also because very small concentrations of phenolics impart a medicinal taste and odor to drinking water. (Beychok, 1967)

Industrial waste waters are processed for removal of organic pollutants by two major categories of treatment: recovery and non-recovery techniques. Use of non-recovery techniques usually results in the pollutant being destroyed by chemical or thermal means. Examples of non-recovery techniques include biological oxidation, direct incineration, and deep well injection. Other examples are carbon adsorption with thermal-oxidative regeneration and liquid-liquid extraction when the solute is destroyed by existing processing steps. (Earhart, 1975)

Recovery techniques employ processing steps to recover the pollutant in a concentrated form. In this way the economic value of the pollutant can offset the costs involved in the waste water treatment. Examples of recovery techniques include steam stripping, liquid
extraction and adsorption onto polymeric or carbon beds employing chemical regeneration. A secondary recovery process to regenerate the solvent and separate the pollutant accompanies the extraction. The cost of recovery techniques are generally higher than non-recovery techniques. This is usually due to the cost of the chemicals and the energy that effect the solvent-pollutant separation. It is seen that the recovered pollutant must be of sufficient quantity and value for the recovery technique to be economically competitive with a non-recovery technique. Phenol is such a pollutant at the concentrations encountered in many waste water effluents.

Most of the recently proposed processes for phenol recovery make use of the chemical nature and physical interactions of the phenol molecule. These processes employ liquid extraction or adsorption. In this study a process is proposed for phenol recovery that offers advantages over previously considered processes. Plant designs suitable for treating a typical coal-gasification quench water stream were used as a basis for comparing the phenol recovery processes.
General Considerations in Liquid Extraction for Waste Water Treatment

Adding an immiscible liquid to another solution containing a given solute results in the solute distributing itself between the two liquid phases. This process proceeds until an equilibrium is established. The two liquids must be immiscible or only partially miscible so that two distinct liquid phases exist. The initial solvent phase is referred to as the feed. It is conventional to refer to the added immiscible liquid as the solvent and the resultant solution of the solute in the solvent as the extract. The residue of the initial phase is the raffinate. The process of bringing immiscible solvents together to allow a solute to distribute in order to obtain a separation is known as liquid-liquid extraction (P. Bailes et al., 1976)

A typical liquid extraction system applied to water treatment is shown in Figure 1. Typically there are three major operations. The overall effect is to separate a waste water feed into a treated stream with a lower solute concentration and a product stream containing the recovered solute. The first operation is the extraction of the solute from the feed into the solvent phase. This is usually accomplished by passing the feed stream countercurrent to the solvent stream in a multistage contactor. The second operation separates the loaded solvent phase, the extract, into solute and solvent streams. The solvent
is recycled back to the contactor. The methods employed to separate the solute from the solvent include a second liquid extraction, evaporation, distillation, chemical reaction and precipitation. The third operation is the recovery of dissolved solvent from the aqueous raffinate stream. Upon leaving the extractor the raffinate will be saturated with the solvent. Recovery may be necessary to reduce solvent loss and prevent contamination of the treated water stream.

Further treatment of the water system may be necessary and biological oxidation is often applied for this purpose. Kiezyk and Mackay [1971] note that the solvent loss is tolerable only in systems where the solubility of the solvent in water is below 10 ppm or where the solvent is very cheap. The most common methods for recovering the solvent are adsorption and gas stripping. Stripping is more effective and less costly with higher volatility solvents. Kiezyk and Mackay [1971, 1973] discuss liquid extraction applied to waste water treatment with particular attention given to phenol removal.

The use of liquid extraction for waste water treatment can offer advantages over other techniques if applied to selected water effluents. Liquid extraction can produce revenue from valuable recovered pollutants, handle non-biodegradable or toxic pollutants and reduce the load to a central biological oxidation unit.
While the cost to treat a given flow of polluted waste water using bioxidation or carbon or polymer adsorption tends to increase as the pollutant concentration increases in the feed, this is not true for liquid extraction. The cost to remove a fixed fraction of pollutants from a given flow of polluted waste water by use of extraction remains approximately constant as the pollutant concentration increases in the feed. Moreover, the revenue generated by the sale of the recovered pollutant increases proportionately with the pollutant feed concentration. Liquid extraction is best applied to selected individual water effluents of high concentration prior to final treatment. Liquid extraction can not compete with biological oxidation or adsorption for processing large quantities of very dilute waste water streams.

Previously, little attention has been given to liquid extraction for waste waters. Earhart [1975] studied this type of recovery process and generalized procedures for applying liquid extraction to selected waste waters. Previous applications include phenol recovery, acetic acid recovery, oily water treatment and desalination. Earhart presented the reasons for the limited use as 1) unacceptably high solvent make-up cost or solvent recovery cost, 2) expense of equipment and energy required for solvent regeneration, 3) the requirement that a large number of alternatives must be considered by the designer in order to
synthesize a good process. (These decisions include the type of solvent, type of extractor, methods of solvent regeneration and solvent recovery.) Finally, 4) the need to identify the chemical nature of the major pollutants present in the waste water in order to evaluate and understand the technique of liquid extraction.

In combined streams the identification of individual pollutants is difficult. For an individual stream with a smaller number of major pollutants present, techniques based on gas chromatography have reduced the problem. These techniques can employ gas chromatography alone or in conjunction with mass spectroscopy or infrared analysis.
Previous Applications of Liquid Extraction for the Recovery of Phenolic Compounds

The large amount of literature written on phenol recovery has been reviewed by Kiezyk and Mackay [1971]. Most processes make use of the -OH functional group of phenol. Fox [1975] and Witt and Forbes [1971] describe processes involving carbon and polymeric adsorption, respectively. The Department of Energy report FE-2240-39 showed typical biological oxidation and adsorption techniques to be less economical than a typical extraction process. This may not be the case for very dilute waste waters. Furthermore, biological oxidation requires special precautions for waste waters containing over 50 ppm phenol to prevent the bacteria from being killed or altered. (McKinney, 1967)

Phenol forms a minimum boiling homogeneous azeotrope with water that contains 9.2 weight percent phenol. (Weast, 1970). For this reason steam stripping is not especially useful for phenol recovery. Liquid extraction appears to be the best method for treating waste waters containing phenol because of the higher costs associated with the alternatives.

Most applications of phenol removal and recovery occur in petroleum refinery wastes, coke-oven liquors and phenolic resin plant effluents. (Kiezyk and Mackay, 1971). Eisenhaur [1968] presents a review of various methods for phenol removal. Previous to 1945 liquid extraction,
adsorption and vaporization were used. Rhodes [1949] describes three types of extraction process in detail. The earliest process used benzene to extract the phenol from the waste water of coke-ovens. The phenol was recovered from the benzene by distillation but the high cost changed the regeneration of benzene to a second extraction with a sodium hydroxide solution. Recovering the phenol in a concentrated sodium phenolate solution is a non-recovery method.

Another process used tricresyl phosphate as the solvent for phenol extraction in order to gain a capacity for phenol in the solvent eight times greater than benzene. The high boiling tricresyl phosphate was separated from the phenol by vacuum distillation. The use of this scheme was short lived as it failed after being tried for a short time in several small plants in Germany. The failure was due to the build up of heavy boiling materials in the solvent which was recirculated to the extractor from the bottoms product of the distillation column. The heavy-boiling organics caused increased viscosity and decreased phenol capacity.

The third liquid extraction process described by Rhodes is the Phenosolvan process. This process is still being used and occasionally improved. The first solvent used was n-butyl acetate. This solvent has three times more capacity for phenol than tricresyl phosphate. Wurm [1968] notes that process changes occurring in the late
1950's included converting to the use of di-isopropyl ether. This change reduced the solubility of phenol in the solvent by 60%. The advantage of this change is the higher solvent volatility. This results in lower costs in solvent regeneration and solvent recovery and was claimed to justify the change.

The solvent recovery operation employed in the Pheno-solvan process is complicated. Figure 2 shows the many processing steps used to recover the solvent. Solvent recovery is necessary since the solubility of di-isopropyl ether in water is about 8000 ppm. The waste water is fed to column A to regenerate a phenol-saturated inert gas stream used in the solvent recovery operation. The waste water leaves column A slightly enhanced in its level of phenol. The main step in the process occurs next as the waste water is passed countercurrent to the di-isopropyl ether solvent stream in the mixer-settler contactor. The raffinate leaves the mixer-settler saturated with di-isopropyl ether. The solvent is removed from this stream in column C, where an inert gas strips the solvent from the water. The water leaves the process purified after leaving column C. The extract stream leaving the mixer-settler is fed to a distillation column, column D, where the phenol leaves as the bottom product and the solvent is recirculated to the mixer-settler as the distillate. This arrangement has a clear advantage over the tricesyl phosphate process because less-volatile compounds leave with
the phenol and no build up occurs in the recirculated solvent. Returning to the solvent-removal operation, it must be noted that the inert gas leaving the stripping column, C, contains solvent and must also be regenerated. For this purpose the inert gas is passed through column B, where the solvent is absorbed by a countercurrent stream of phenol obtained from the distillation column bottoms product. This phenol is then returned to the stripping section of the distillation column. The inert gas leaving column B, now saturated with phenol, is passed countercurrent to the waste water feed in column A, where the phenol is absorbed by the water. The waste water is next fed to the mixer-settler and the inert gas stream, now saturated with water, is recycled back to column C to strip the solvent from the mixer-settler raffinate stream.

High capital costs and moderate operating costs characterize the Phenosolvan process. The bulk of the operating cost is contributed by the cost of supplying heat for the separation in the distillation column.

A recent process for phenol recovery was described by Laurer et al. [1969]. Chem-Pro Equipment Corporation licenses this process, which employs an undisclosed proprietary solvent. Figure 3 represents the processing scheme. The waste water is fed to a Karr reciprocating plate extractor. Mulligan and Fox [1976] report that the high capacity of the solvent allows the use of the very low solvent-to-
waste water ratio of 1:18. Phenol removal efficiencies are reported to be in the 99.7-99.9% range. The extract is regenerated in a distillation column with the solvent being recirculated to the extractor from the overhead product. The solvent removal operation is much simpler than that of the Phenosolvan process. The raffinate stream is fed to a steam-stripping column. This stream leaves the stripper purified and the solvent goes overhead accompanied by water vapor. The stripper overhead is condensed, forming two phases. The solvent phase is recycled to the extractor and the water phase is returned to the stripper.

Compared to the Phenosolvan process the capital costs for the Chem-Pro process are low. The major operating cost is due to the steam required in the stripper. The energy required to distill the solvent from the phenolics is lower than in the Phenosolvan process because of the lower solvent flow employed by the Chem-Pro process.

Earhart et al. [1977] proposed dual solvent extraction for phenol recovery. Fox [1975] described a process of the Rohm and Haas Co. for recovering phenol by using polymeric adsorption with chemical regeneration of the adsorbent beds. Department of Energy Report # FE-2240-39 compared this process with biological oxidation and the Chem-Pro process and found the adsorption process to be the least economical for the case evaluated.
General Considerations in Solvent Selection for Phenol Recovery

Publications dealing with solvents for phenol extraction from waste water include Kiezyk and Mackay [1971,1973] and Lowenstein-Lom et al. [1947].

The unit operations of which a chemical process is composed dictate certain definite properties a solvent should possess. The normal specification for an extraction problem is to specify the feed rate and composition and to require that the concentration of undesired solute be reduced to a specified level. The design of extraction units is concerned with two areas. (Kiezyk and Mackay, 1971). First is to determine the number of stages required for the contactor. The number of stages is primarily dependent on the degree of separation required. Second is the design with respect to the transport phenomena that determine the size and internal configuration of the extraction vessel.

The distribution coefficient, $K_D$, is a property of the solvent-solute-water system. It influences the number of stages required and the solvent flowrate for a desired separation. The distribution coefficient is defined as

$$K_D = \frac{x_1}{x_2} = \frac{\gamma_2}{\gamma_1}$$

where $x$ is the mole fraction of solute and $\gamma$ is the activity coefficient. The subscripts refer to the phases in equilibrium. At equilibrium the fugacities of the solute in each phase are equal. The fugacity, $f$, is the product of the
mole fraction $x$, the activity coefficient $\gamma$ and the reference fugacity $f^\circ$ (the fugacity of the pure solute at the same temperature and pressure). Because the reference fugacities are identical the distribution coefficient $K_D$ is equal to the ratio of activity coefficients. (Prausnitz, 1969)

Increasing the distribution coefficient allows a lower number of stages and a lower solvent flow for a specified separation. It can be seen from the definition of the distribution coefficient that a high $K_D$ is obtained by having a small activity coefficient for the solute in the solvent phase. The activity coefficient is a measure of how badly the solute would like to escape from the phase. The activity coefficient is dependent on temperature and concentration. For phenol removal it is desired to have a solvent that will associate with the phenol but not associate with itself or the water. Unfortunately, the properties of a solvent that promote association with phenol generally increase the solubility of the solvent in water. This results because both phenol and water can associate through hydrogen bonding with a polar group on a solvent molecule. Increased solvent solubility in water results in higher solvent losses or a higher separating agent requirement for solvent recovery. A low solubility of water in the solvent is desired but is not critical.

The distribution coefficient and mutual solubilities change as functions of temperature. Data for these proper-
ties must therefore be obtained at the temperature for which the commercial extraction would operate. The distribution coefficient also depends on solute concentration in the solvent phase. This is because solute molecules must compete for an association with the available solvent molecules. Greminger [1979] has obtained data for the Phenol-Water-Di-isopropyl ether (DIPE) system. Also obtained were data for systems involving di-hydric phenols in water and DIPE and MIBK as solvents. The data consist of distribution coefficients at constant temperature as a function of the pH of the water phase. The water-phase concentration was kept approximately constant at 5000 ppm. It was shown that the distribution coefficient dropped significantly at levels of pH above 8 in the aqueous phase. MIBK was shown to have a higher capacity for phenolics than DIPE at every pH. Typical waste waters from coal gasification plants have phenol concentrations as high as 5000 ppm and have a pH of about 9. The waste waters are well buffered by NH$_3$ and CO$_2$. At higher pH values more of the phenol is ionized. The phenolate ion is not extracted by the solvent, thus accounting for the lower distribution coefficients. The implication is that any physical solvent for the extraction of phenol from waste water could exhibit a similar decrease in the distribution coefficient at high pH. Previous investigators have not examined the effect of pH on the distribution coefficient for phenol. Kiezyk and Mackay [1973] do, however, note that the ionization of phenol in water is
not appreciable at concentrations below 1000 ppm and a pH of 11.

The density of a solvent should differ by 10% or more from that of the aqueous phase to facilitate counter-current flow of the two phases in an extractor. A high interfacial tension also promotes rapid separation of the phases. The formation of emulsions in the system is clearly undesired. A solvent should by preference also have a low viscosity to improve mass-transfer rates.

The flashpoint of the solvent should be high and its toxicity should be low. It is also important that the solvent be chemically inert except where a reversible reaction could be used to promote the specified separation. In waste water treatment hydrolysis is definitely unwanted.

Solvent regeneration is aided by a low boiling point and a low heat of vaporization. For certain solvent regeneration schemes it is necessary for the overhead product to be the solvent and the solute to be the bottoms product. In this way high boiling impurities are removed from the process with the solute. For waste water treatment solvents with normal boiling points in the range of 115°-135°C are the most suitable. In waste water treatment the potential problems associated with having the solvent as a contaminant in the final effluent must also be considered.

The desirable characteristics of a solvent for waste water treatment are summarized as follows:
16.

1. High distribution coefficient, \( K_D \)
2. Low mutual solubility for the solvent and water
3. Solvent boiling point in 115°-135°C range
4. Chemically inert
5. Appreciably different density than water, low viscosity, high interfacial tension
6. High flashpoint and low toxicity
7. Low cost

Good candidates for a solvent for phenol recovery can be selected from families of solvents by applying these criteria. Lowenstein-Lom et al. state that a solvent combining all or most of these characteristics would probably be polar, have a high dielectric constant and be nonionizing. Halogenated solvents are excluded by their low distribution coefficients. The sulfur atom will generally raise the boiling point too high. The required polarity is usually achieved with an oxygen atom in the solvent molecule.

The work of Abrams and Prausnitz [1975] and Won and Prausnitz [1975] shows that polar organic fluids are superior to nonpolar hydrocarbons for removal of phenolic solutes from water by liquid extraction. The disadvantage of polar solvents is their greater solubility in water compared to hydrocarbons. Because a good solvent should hydrogen-bond with phenol but not with itself, esters, ethers and ketones are promising polar organic solvents. A polar solvent is usually more expensive than a nonpolar
solvent and dilution of the polar solvent with a nonpolar solvent may be desirable. Medir and Mackay [1975] point out that the amount of polar solvent dissolved in the water stream may be reduced if a diluted solvent is used. Medir and Mackay, Nakagawa and Karenman have published data on mixed solvents. A synergistic effect exists for some solvent mixtures due in part to the formation of mixed solvates. This effect is evidenced by the positive deviation from additivity of the distribution coefficient for mixed solvents.

Most alcohols are ruled out as solvents by a high solubility in water on one hand or high boiling point on the other. Certain secondary alcohols meeting the other criteria have unfavorable distribution coefficients.

Certain aliphatic esters can meet nearly all of the requirements of a good solvent. Secondary esters have nearly the same extracting power for phenol as do primary esters, but tertiary esters have unfavorable distribution coefficients. The main drawback in the use of aliphatic esters is their ease of saponification. Butyl acetate is reported by Lowenstein-Lom et al. to be saponified by ammonia in liquors with a free ammonia concentration higher than 3 g/liter.

Many ethers have relatively favorable distribution coefficients for phenol. Use of the higher symmetrical ethers promotes the extraction of the polyhydric phenols. The high vapor pressure of some ethers may lead to high
losses. The low flashpoints and high inflammability of ethers are also against their use.

Ketones offer good distribution coefficients and do not hydrolyze. They can be used for waste streams containing high concentrations of ammonia, which are typical of the effluents expected from coal gasification quenches. Ketones can be chosen that have boiling points, densities and water solubilities in the desired range.

From an environmental viewpoint it can be concluded that esters, ethers and ketones are acceptable solvents. (Kiezyk and Mackay, 1973). Biological oxidation of alcohols, esters and ketones is rapid. Hydrocarbons and chlorinated hydrocarbons do not oxidize as well. This is a consideration because waste water treated by a liquid extraction process is often followed by biological oxidation to achieve very low solute levels. Bioassay studies show no alcohol or ketones to be toxic in concentrations below 500 mg/liter unless chlorinated. (Kiezyk and Mackay, 1973)

Experimental Procedure

After preliminary screening of solvents, methyl isobutyl ketone (MIBK) was chosen as the solvent to study. The mutual solubility of MIBK and water was determined at three temperatures. The distribution coefficient of phenol between MIBK and H₂O was observed at the same three temperatures as a function of phenol concentration.

For the determination of distribution coefficients solutions of MIBK and phenol were prepared in a range between 5 and 20 weight percent phenol. For mutual solubility studies pure MIBK was used. Reagent-grade chemicals were used without further purification except when calibrating instruments. Approximately 10 ml of the organic solution was allowed to equilibrate with an equal volume of water in an equilibration tube. The equilibration tube was a cylindrical pyrex tube 2.5 cm in diameter and 12 cm in length. The equilibration tube was sealed with a ground glass stopper. A stretched rubber band held the stopper on and insured a tight seal. The tube was placed in a holder and immersed in a constant temperature bath (CTB). The tube was rotated around its horizontal axis allowing the two phases to mix turbulently for at least two hours. It was shown that equilibrium was attained in this length of time. The rotation was then stopped and the phases were allowed to settle in the CTB for at least four hours. At the beginning of the settling time the glass top was replaced with a rubber septum. Samples for analysis were removed
from the equilibration tube using a gas chromatography syringe. In this way the sample was maintained at the temperature of interest until just before injection into a gas chromatograph. A long-needled syringe was used to sample the aqueous phase. Air was bubbled out through this needle as it was lowered through the organic phase. This prevented organic solvent from being collected in the needle in the process of obtaining a sample from the aqueous phase.

Gas chromatography was used to determine the equilibrium mass fractions of solute, solvent and water in the aqueous and organic phases. The Varian Aerograph model 90-P gas chromatograph, with thermal conductivity detector, used a stainless-steel column two meters long and 3.18 mm in diameter filled with Porapak Q. Helium was used as carrier gas. The aqueous (1 μl) and organic (2.5 μl) samples obtained directly from the equilibration tube were injected immediately to obtain the chromatograms. At least seven samples were analyzed for each distribution coefficient.

The gas chromatograph was calibrated with standard aqueous and organic solutions having compositions similar to those of the experiment. For the preparation of these standard solutions the MIBK was first dried over molecular sieve adsorbent. The chromatograms obtained for these solutions provided calibration of the relative response of the detector for known mass fractions of MIBK, water
and phenol.
Experimental Results

Mutual solubilities were determined for the MIBK-water system at three temperatures. These results and other reported values are listed in Table 1.

Table 1. Mutual solubility for MIBK-water system at 30.0°, 50.0°, and 75.0°C (mass fractions).

<table>
<thead>
<tr>
<th></th>
<th>MIBK in H₂O Phase</th>
<th>Other Investigators</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Expt.</td>
<td>1</td>
</tr>
<tr>
<td>30.0°C</td>
<td>.0182</td>
<td>.0164</td>
</tr>
<tr>
<td>50.0°C</td>
<td>.0146</td>
<td>.0139</td>
</tr>
<tr>
<td>75.0°C</td>
<td>.0137</td>
<td>.0135</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>H₂O in MIBK Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.0°C</td>
<td>.0204</td>
</tr>
<tr>
<td>50.0°C</td>
<td>.0244</td>
</tr>
<tr>
<td>75.0°C</td>
<td>.0284</td>
</tr>
</tbody>
</table>

¹Gross, Rintelen and Saylor [1938]
²Ginnings, Plonk and Carter [1940]
³Narasimhan et al. [1962]

The decreasing solubility of MIBK in water with increasing temperature indicates a decrease in hydrogen bonding between MIBK and water. At higher temperatures more energy is available in the solution to break hydrogen
The effect of mass fraction of solute on the distribution coefficient of phenol between water and MIBK is shown for three temperatures in Figure 4. The distribution coefficient, \( K_W \), is defined as

\[
K_W = \frac{W_S}{W_w}
\]

where \( W_S \) is the mass fraction of solute in water-free solvent and \( W_w \) is the mass fraction of solute in water.

Won and Prausnitz [1975] examined distribution coefficients of several phenolic solutes of concern to waste water treatment at high dilution at 25°C. The solvents examined were butyl acetate and MIBK. For every solute examined the distribution coefficient was higher in MIBK than in butyl acetate. The data is listed in Table 2.

Table 2. Distribution coefficients, \( K_W \), for phenolic solutes between water and MIBK at high dilution at 25°C. (Won and Prausnitz, 1975)

<table>
<thead>
<tr>
<th>Solute</th>
<th>( K_W )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>110</td>
</tr>
<tr>
<td>m-Cresol</td>
<td>264</td>
</tr>
<tr>
<td>3,5-Xylenol</td>
<td>814</td>
</tr>
<tr>
<td>Pyrocatechol</td>
<td>20.3</td>
</tr>
<tr>
<td>(o-Dihydroxy phenol)</td>
<td></td>
</tr>
<tr>
<td>Resorcinol</td>
<td>15.2</td>
</tr>
<tr>
<td>(m-Dihydroxy phenol)</td>
<td></td>
</tr>
<tr>
<td>o-Chlorophenol</td>
<td>490</td>
</tr>
</tbody>
</table>

Narasimham et al. [1962] reported a study of solubility and equilibrium for the phenol-water-MIBK system at 30.0°C.
They found that the densities of the aqueous phase and organic phase are nearly equal at 30°C for a phenol concentration of 64.5 to 70.8 weight percent in the extract phase. This indicates that a practical extraction could be carried out with an extract stream that is perhaps as concentrated as 50% phenol. With such a high concentration, energy would be saved in solvent regeneration and the distribution coefficient for other phenolic solutes would be enhanced by the high phenol concentration in the organic phase.
A Low Energy Phenol Recovery Process

A goal of this work was to develop a process for the recovery of phenol from waste water that uses significantly less energy than those described previously. The flowsheet for the proposed process is shown in Figure 5. The three major steps in the process are not novel: liquid-liquid extraction is used to separate the phenol from the waste water with a solvent, distillation regenerates the solvent and leaves the phenol as product, and steam stripping recovers residual solvent from the treated water stream. The reduction in energy usage results from the way that these steps are carried out.

The waste water of interest originates from the quench step in coal gasification and is typically at a temperature of 75° to 80°C. It is advantageous to cool this water before the liquid-liquid extraction step because the capacity of the solvent is higher at lower temperature. The heat extracted is used to generate the steam for the steam stripper, the operation of which is described later.

The solvent used in the liquid-liquid extraction unit is MIBK. This solvent has been shown to have a high capacity for phenol and, in addition, has a relatively low heat of vaporization. The extract steam from the liquid-liquid extraction unit will contain 20 to 30% phenol by weight. Regeneration of the MIBK in the distillation column will require relatively little energy due to the high ratio of solvent to phenol fed to the column and the
low heat of vaporization of the solvent. Additionally, the large separation factor for MIBK-phenol means that the reflux will not be large. To minimize the energy lost as sensible heat, the distillation column can be operated under vacuum, at the pressure for which the MIBK-water azeotrope is able to be condensed with the available cooling water. In addition, the bottoms product can be used to preheat the column feed.

The flow of water through the steam stripper is large. The stripper must be designed carefully to avoid a substantial loss of energy in the form of sensible heat in the outlet liquid. The use of a vacuum steam stripper as a general method of removal of small amounts of volatile organic materials from waste water streams was considered by Rasquin et al. [1978]. The most important variable of such a process was found to be the stripping steam flow. This is because for organic compounds of moderate volatility and limited solubility, a satisfactory degree of stripping can be achieved in relatively short and inexpensive columns. The high activity coefficients of the organic in the water provides a large driving force for mass transfer. Moreover, the steam flow for a given degree of stripping was found to exhibit a minimum value as column pressure was varied for a set feed stream temperature. The same minimum was shown to exist as the feed stream temperature was varied for a set column pressure. Since
the driving force for mass transfer is more than adequate, further increase of the steam flow above the minimum is only marginally useful. The minimum steam flow is set almost entirely by the energy balance for the process while the degree of stripping is determined by column length. The steam requirement is the sum of the flows to supply the following needs:

1. The energy necessary to vaporize the organic material
2. The steam necessary to accompany the organic vapor from the top of the column
3. The energy to heat the remaining water to exit temperature at the bottom of the column

It is the second requirement which primarily determines the cost of the process.

The differential equations that describe the heat and mass transfer occurring when a volatile, sparingly soluble organic compound is steam stripped from water in a vacuum column were presented by Rasquin et al. [1978]. A computer program was developed to solve the equations simultaneously by a finite-difference method. A column using packing similar to 2-inch Pall rings was modelled. This program was modified slightly and applied in this work for the MIBK-water system. The program is described in Appendix A. Whereas Rasquin examined the optimum operating pressure for a given feed stream temperature, this work determines the optimum feed temperature for a chosen column pressure. The program was used to simulate column behavior in order to
choose other process operating conditions which are described in the discussion that follows.

a. Effect of Varying Steam Flow

The character of stripper operation as a function of steam flow is shown in Figure 6. The residual MIBK in the exit water is seen to change only very slowly with steam flow as the flow is decreased from a relatively high value and then to increase dramatically as the steam flow reaches a certain value, the minimum value. The same pattern is found for each of the three column pressures examined 5.07, 9.56 and 12.61 kN/m² (53.89, 71.67 and 94.61 torr). Clearly, if steam economy is of overriding importance to the process, then no matter what pressure of operation is chosen, the column should be operated near the minimum steam flow. The steam flow should be sufficiently above the minimum that perturbations in the operation would not result in large changes in the residual MIBK concentration. However, it should be noted that the gain in stripping from increasing the steam flow diminishes rapidly once the flow is of the order of 10% above the minimum value. Increasing column length is the most effective method for increasing the degree of stripping when steam flow is known to be adequate.
b. Effect of Column Pressure

Figure 6 also shows that in terms of steam flow there is little to be gained by varying the pressure of the column while maintaining the optimum feed temperature at each pressure. The highest pressure examined requires the least amount of steam flow, but the difference in the minimum steam flow between 5.07 kN/m² (53.89 torr) and 12.61 kN/m² (94.61 torr) is only 7.5%.

c. Effect of Feed Stream Temperature

In establishing the operating conditions for each of the column pressures considered in Figure 6, the feed temperature was chosen to be the boiling point of pure water at the pressure at the top of the column where the feed is introduced. Pressure drop from the bottom to the top of the column was included in the calculations. This choice of feed temperature is a result of the studies of Rasquin, who found that for a fixed feed temperature, the minimum steam flow decreased as column pressure was lowered from relatively high values toward the vapor pressure of pure water at the feed temperature. Operation below this pressure would result in simple flashing of the feed as it is introduced into the top of the column. The effect would be to operate with a feed exactly at the boiling point of water at column pressure, but at a temperature corresponding to the lower pressure. Such operation would result in no additional stripping but would simply increase
the load on the overhead condenser of the stripper. The optimum operation for a vacuum steam stripping column is thus at a pressure equal to the vapor pressure of water at feed temperature. At this point the minimum possible steam flow is required. Alternately, if the pressure of the column is chosen, the optimum feed temperature is the boiling point of water at that set pressure.

d. Other Considerations

The process shown in Figure 5, and described previously, is, however, not highly restricted in the choice of steam flow. The waste heat of the quench stream generates a flow of steam at the bottom of the column that is well above the minimum shown in Figure 6 under all conditions studied. Other considerations now enter in the choice of column pressure and feed temperature.

The maximum pressure of operation is fixed by the temperature of the quench stream used to generate the steam in the stripper reboiler. As the column pressure is increased, the approach temperature in the reboiler is reduced because the bubble point of the exit stream increases. The minimum operating pressure is fixed by the available cooling water temperature. If this temperature is taken to be 35°C the resulting temperature of condensation can be taken as about 40°C. The vapor pressure of the heterogeneous MIBK-water azeotrope that condenses is then 9.56 kN/m² (71.67 torr) and this column pressure can be chosen in considering the
process further.

Because of the availability of ample waste heat, the question of lowering the feed temperature below the boiling point of water at 9.56 kN/m\(^2\) (71.67 torr) was examined, despite the knowledge that such a change would increase the steam requirement. The results of these calculations are shown in Figure 7. Pressure is fixed at 9.56 kN/m\(^2\) (71.67 torr), and the feed temperature is varied from 44.896°C down to 39.519°C. The minimum steam flow requirements increase as the feed temperature is lowered to 5°C below the boiling point. The energy balance requires a greater amount of sensible heat to be provided to the exit stream as the feed temperature is lowered. None of the increase is required by the mass balance to effect mass transfer. However, the amount of steam required is still within that available in the waste heat of the quench stream throughout the range of feed temperature considered.

A lower feed temperature requires that more heat be transferred in the reboiler, resulting in an increase in cost for the greater heat exchanger area required. However, it reduces the heat exchange area required in the overhead condenser. Despite the fact that more steam is generated at the bottom of the stripper, the vapor leaving the top of the stripper is reduced as the feed temperature is reduced. Figure 8 shows this clearly. The excess steam has
gone largely into heating the water from the feed temperature to the bubble point temperature at the bottom of the column. The vapor leaving the top of the column is cooled by the colder feed, and the amount of water vapor accompanying the vaporized MIBK is less. This is because at the lower temperature the vapor pressure of water is lower. The heat exchange area of the condenser is thus reduced, and the cooling water requirements are also lowered.

A high column pressure decreases the cost of the overhead condenser while a low pressure decreases the reboiler cost. This is due to the temperature approach available in each heat exchanger. By balancing costs the vacuum steam stripper was chosen to operate at a top column pressure of 12.61 kN/m² (94.61 torr) and a feed temperature of 45°C.

It is seen that operating under vacuum has two advantages. First, the steam required for sensible heat is reduced because the exit stream bubble point temperature is lowered. Second, a lower temperature quench stream is able to maintain the temperature approach in the reboiler needed to generate the stripping steam.
General Applicability of Vacuum Steam Stripping

Vacuum steam stripping is best applied to aqueous streams containing low concentrations of volatile organic material. The properties of the dissolved organic compound are the most critical to the successful use of vacuum steam stripping. One important property of the organic material is its solubility in water. As low a solubility as possible is desired. The steam requirement is proportional to the solute loading in the feed. The required length of the column is also indicated by the solubility because a low solubility in a phase indicates a high activity coefficient. A high activity coefficient increases the driving force for mass transfer and thus lowers the required column length. A low solubility also insures that the overhead vapor will condense to form two phases. The aqueous phase is, of course, recycled back to the stripper feed stream. Without the final separation provided by the formation of separate phases the enrichment would not be sufficient for the use of steam stripping.

Another important property of the organic compound is the vapor pressure. The vapor pressure of the compound must be low enough to allow condensation of the overhead vapor. The minimum total column pressure is set by this requirement. Di-isopropyl alcohol is a poor candidate for steam stripping due to its high vapor pressure, even though it is an acceptable solvent for phenol recovery. The loss of
organic compounds through the vacuum system is reduced for compounds with lower vapor pressures. On the other hand, a higher vapor pressure increases the driving force for mass transfer. It is desired that the organic compound have a low heat of vaporization since this has an effect on the steam requirement.

As was previously stated, the feed stream temperature is important. The steam requirement is the minimum when the feed is at the saturation temperature of water for the total column pressure. For a slightly increased steam requirement the capital cost for the overhead condenser can be reduced if the feed temperature is below the saturation temperature of water. If the feed is not available near the saturation temperature, the steam requirement for steam stripping will be excessive. For the case which employs a process stream to supply the heat for steam generation, the process stream must possess the total amount of heat required and have a high enough temperature to maintain the required temperature approach in the reboiler. In effect, the temperature available for the process stream determines the maximum total column pressure.
Economic Comparison of Phenol Recovery Processes

Preliminary cost evaluations were used to compare the Low Energy process described in this work to the Pheno-solvan and Chem-Pro Processes. The three processes were sized to treat a specified water stream containing phenol. The water stream had a composition similar to the combined condensate from the raw gas quench and shift conversion operations of a coal gasification plant. The phenol concentration was assumed to be 15,800 ppm. The stream flow and concentration are the same as those considered in DOE report FE-2240-39 for a plant producing $250 \times 10^9$ BTU/day of pipeline-quality gas from western coal.

Most coal-gasification plants produce process condensates containing about 5,300 ppm of phenols. The 15,800 ppm value was based on preliminary pilot-plant data for the Steam-Oxygen process. The PERC Synthane process reports a similar level of phenol. In these processes the coal is fed to the gasifier as a slurry using recycled process condensate for coal feeding. The higher level of phenol results from the buildup of phenols in the gasifier. Two-thirds of the process condensate is recycled so that the amount of process condensate treated is reduced to approximately 226,800 kg/hr for a $250 \times 10^9$ BTU/day plant.

The higher phenol concentration is advantageous for all three of the processes compared below because they all employ extraction. However, all three processes can
treat levels of phenol found in present coal gasification plants (5,300 ppm) and coke oven wastewater (1500 ppm).

In preparing the cost estimate the following assumptions were made:

1. Quench water contains 15,800 ppm of phenol.
2. Extraction removal is 99.9% of the phenol in the quench water.
3. Quench water flow rate is 227,000 kg/hr (1000 gpm). This corresponds to a production of $250 \times 10^9$ BTU/day of pipeline-quality gas from western United States coal.
4. Quench water temperature is 70°C.
5. To achieve higher reliability the phenol recovery units are split into two trains. Each train treats 50 percent of the total capacity. No spare trains are needed.
6. Regenerated solvent contains no phenol.
7. Cooling water is available at 30°C.
8. Liquid hold-up is 3 minutes in the bottoms of distillation columns and 10 minutes in the reflux tanks.
9. Extractors are multiple-stage mixer-settlers with solvent recycle to obtain the desired aqueous feed-to-solvent ratios in mixers. A stage efficiency of 85% was assumed and mixer-settler costs were estimated from the equations of Treybal [1963].
10. An overall heat-transfer coefficient of \( 1135 \, \text{Wt/m}^2 \, {}^\circ\text{K} \) (200 BTU/hr-ft\(^2\)-°F) was used in the condensers and reboilers. For the heat exchange between aqueous streams and between aqueous and organic streams, overall heat transfer coefficients were assumed to be \( 1420 \, \text{Wt/m}^2 \, {}^\circ\text{K} \) (250 BTU/hr-ft\(^2\)-°F) and \( 284 \, \text{Wt/m}^2 \, {}^\circ\text{K} \) (50 BTU/hr-ft\(^2\)-°F).

11. The by-product for phenol was taken as 15 cents per gallon. This price is for a crude phenolic mixture. For comparison, Chemical Marketing Reporter lists commercial-grade phenol at $0.15 per pound in the 4th quarter of 1978.

12. An on-stream factor of 90 percent was used.

13. All costs are in 4th-quarter 1978 dollars. (M & S index for chemical industries = 560.4.)

14. The operating labor was assumed to be one-fourth man per shift for the Low Energy and Chem-Pro processes and one-half man per shift for the Phenosolvan Process.

15. Carbon steel is assumed to be adequate for all pieces of equipment.

16. Only solvent (not pollutant) inventories were included in the working capital.

17. The diameter of the distillation columns was sized for a superficial vapor velocity of 6 ft/sec.
Together with these assumptions, the methods discussed in Appendix E were used to estimate the capital and operating costs for each of the three processes. The capital costs are listed in Table 3 and the operating costs are listed in Table 4. Table 5 presents a material balance for the Low Energy process proposed in this work.

A comparison of capital costs shows the Low Energy process to be higher by 7.3% than the Chem-Pro process, which has the lowest capital cost. The estimate for the Phenosolvan capital costs is conservatively low because the exact nature of the heat exchange and solvent recovery operation was not known. Because the solvent used in the Chem-Pro process is of unknown composition, being proprietary, the solvent was assumed to have the same physical properties as MIBK.

The Low Energy process is seen to have a significant advantage over both the Phenosolvan and Chem-Pro processes. The treatment cost is 40% lower than the cost for the Phenosolvan process and 70% lower than either of the two other processes. Although the Low Energy process requires more cooling water than the Phenosolvan process, the effluent water could be recycled through a cooling tower to supply its entire cooling water requirement. Other considerations which recommend the use of the Low Energy process are as follows:
### Table 3. Capital Costs for Phenol Recovery

<table>
<thead>
<tr>
<th>Capital Cost</th>
<th>Low Energy Process</th>
<th>Phenosolvyan</th>
<th>Chem-Pro</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Plant Investment (TPI)</td>
<td>$3,252,500</td>
<td>$3,723,325</td>
<td>$3,032,420</td>
</tr>
<tr>
<td>Equipment Item</td>
<td>Percent of Total</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Extractor</td>
<td>23.7</td>
<td>34.0</td>
<td>32.2</td>
</tr>
<tr>
<td>Distillation Column</td>
<td>6.9</td>
<td>2.5</td>
<td>3.9</td>
</tr>
<tr>
<td>Solvent Recovery Columns</td>
<td>7.2</td>
<td>6.9</td>
<td>3.8</td>
</tr>
<tr>
<td>Heat Exchangers</td>
<td>24.8</td>
<td>22.6</td>
<td>9.4</td>
</tr>
<tr>
<td>Pumps &amp; Drives</td>
<td>8.7</td>
<td>11.8</td>
<td>10.3</td>
</tr>
<tr>
<td>Vacuum System</td>
<td>1.2</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Offsite Facilities</td>
<td>27.5</td>
<td>22.2</td>
<td>40.4</td>
</tr>
</tbody>
</table>

**NOTE:** Plant Capacity is 115,290 kg/hr of quench water containing 15,800 ppm of phenol. This corresponds to $250 \times 10^9$ BTU/day of pipeline-quality gas from western coal. The on-stream factor was taken as 90 percent. Costs are in 1978, 4th-quarter dollars; M & S chemical index = 560.4.
Table 4. Operating Costs for Phenol Recovery

<table>
<thead>
<tr>
<th>Annual Operating Costs</th>
<th>Low Energy Process</th>
<th>Phenosolvan</th>
<th>Chem-Pro</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Gross Operating Cost</td>
<td>$1,626,105</td>
<td>$1,854,855</td>
<td>$2,023,900</td>
</tr>
<tr>
<td>Phenol By-Product Credit</td>
<td>$1,066,580</td>
<td>$1,066,580</td>
<td>$1,066,580</td>
</tr>
<tr>
<td>Total Net Operating Cost</td>
<td>$ 599,525</td>
<td>$ 788,275</td>
<td>$ 957,320</td>
</tr>
<tr>
<td>Total Net Cost of Treating 1000 Gal.</td>
<td>$ 1.17</td>
<td>$ 1.64</td>
<td>$ 2.00</td>
</tr>
</tbody>
</table>

Utilities

<table>
<thead>
<tr>
<th></th>
<th>Percent of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>13.9</td>
</tr>
<tr>
<td>Electricity</td>
<td>3.5</td>
</tr>
<tr>
<td>Cooling Water</td>
<td>6.8</td>
</tr>
<tr>
<td>Solvent Cost</td>
<td>1.7</td>
</tr>
<tr>
<td>Labor Cost</td>
<td>1.9</td>
</tr>
<tr>
<td>Labor-Dependent Costs</td>
<td>2.2</td>
</tr>
<tr>
<td>TPI-Dependent Costs</td>
<td>70.0</td>
</tr>
</tbody>
</table>

NOTE: Plant Capacity is 115,290 kg/hr of quench water containing 15,800 ppm of phenol. This corresponds to 250\times10^9 BTU/day of pipeline-quality gas from western coal. The on-stream factor was taken as 90 percent. Costs are in 1978, 4th-quarter dollars, M & S chemical index = 560.4.

The following ratios of aqueous feed to recycled solvent were assumed:

- Low Energy Process 13.3:1
- Phenosolvan Process 10.0:1
- Chem-Pro Process 13.3:1
Table 5. Material Balance for Low Energy Process for Phenol Recovery

<table>
<thead>
<tr>
<th>Stream</th>
<th>Temperature (°C)</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (kN/m²)</td>
<td>206.8</td>
<td>193.0</td>
<td>193.0</td>
<td>193.0</td>
<td>12.61</td>
<td>13.02</td>
</tr>
<tr>
<td></td>
<td>Condition</td>
<td>liq.</td>
<td>liq.</td>
<td>liq.</td>
<td>liq.</td>
<td>vap.</td>
<td>liq.</td>
</tr>
<tr>
<td>Water (kg/hr)</td>
<td></td>
<td>113,400</td>
<td>113,400</td>
<td>113,400</td>
<td>113,230</td>
<td>1,019</td>
<td>113,400</td>
</tr>
<tr>
<td>MIBK (kg/hr)</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1,675</td>
<td>1,731</td>
<td>2</td>
</tr>
<tr>
<td>Phenol (kg/hr)</td>
<td></td>
<td>1,826</td>
<td>1,826</td>
<td>1,826</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Stream</th>
<th>Temperature (°C)</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (kN/m²)</td>
<td>193.0</td>
<td>165.4</td>
<td>193.0</td>
<td>146.1</td>
</tr>
<tr>
<td></td>
<td>Condition</td>
<td>liq.</td>
<td>liq.</td>
<td>liq.</td>
<td>liq.</td>
</tr>
<tr>
<td>Water (kg/hr)</td>
<td></td>
<td>373</td>
<td>373</td>
<td>203</td>
<td>≥0</td>
</tr>
<tr>
<td>MIBK (kg/hr)</td>
<td></td>
<td>6972</td>
<td>6972</td>
<td>8647</td>
<td>≥0</td>
</tr>
<tr>
<td>Phenol (kg/hr)</td>
<td></td>
<td>1824</td>
<td>1824</td>
<td>≈0</td>
<td>1824</td>
</tr>
</tbody>
</table>

NOTE: Material balance is for one of two 50% trains.
1. The cost of solvent regeneration through distillation can be further reduced by operating the extraction step in the process to produce a higher concentration of phenol. In this way, the heat required per pound of phenol recovered would be diminished. The equilibrium data obtained in this study do not extend to such high concentrations, but such an operation would appear feasible.

2. MIBK has a capacity for phenol that is superior to that of DIPE at higher pH levels and has a much higher capacity for polyhydric phenols as well (Greminger, 1979).

3. The Low Energy process is less complex and would occupy less area than the Phenosolvan process.

4. The treatment cost for the Low Energy process could be reduced further if the process condensate stream temperature was higher and if the available cooling water temperature was lower. The cost comparison was conducted for the worst possible case of a process condensate temperature of 70°C and a cooling water temperature of 30°C. Process condensate temperatures are typically as high as 80°C and higher. Alternately, a cooler process condensate could be used to condense the distillation overhead stream to raise the process condensate temperature before supplying the heat in the vacuum steam stripper. Whereas a higher process
condensate temperature reduces the cost of the Low Energy process, the Phenosolvan process suffers.

5. Since the Low Energy process uses less steam and electricity than either the Phenosolvan or Chem-Pro processes, it would appear that the advantage would be enhanced in the future as the cost of energy increases.

Useful information on the Phenosolvan process was obtained from Jauernik [1960], Wurm [1968, 1968] and Beychok [1974]. For the Chem-Pro process, information was available from Lauer, et al. [1969], Chemical Processing, volume 40, number 10, September 1977, and DOE report FE-2240-39.
Appendix A

Steamp Stripper Calculation Procedure
In Appendix A the mathematical model employed to predict the performance of a packed column is detailed. The model is designed for columns in which sparingly soluble, volatile organic liquids are removed from water by steam stripping, normally under vacuum. The model is written to handle up to four organic components; however, the calculations have been done only for systems containing a single organic component. The packed column is considered to be a differential contactor, and for purposes of analysis is segmented lengthwise into a set of discrete, differential elements. Figure A-1 represents this concept.

As Figure A-1 shows, the length of the column, \( Z \), is broken into an arbitrary number of differential elements. If the size of the differential element is small enough it can be assumed that an average or midpoint value of a function can be evaluated and used to approximate the function across the whole element. There are \( N_J \) boundaries for the differential element, so, therefore, there are \( N_J-1 \) differential elements. The differential elements are of length \( \Delta z = Z/(N_J-1) \). \( z_{J-1} \) is used to indicate the midpoint of the differential element with boundaries at \( J-1 \) and \( J \). \( z_0 \) indicates the midpoint of any differential element in the column.

As a first step in building the model, the variables of interest must be identified. For the packed column the variables to be examined are \( T_L, T_V, L, V, P, x_i, x_w \).
$y_i$ and $y_w$. For the case of one dissolved component this amounts to nine variables. These nine variables are to be tracked at every point down the length of the column. Therefore, the solution will be comprised of a value for each variable at each $J$ position bounding the differential elements. In order to obtain the solution for the nine variables, nine equations which express the relationships between the variables are required. The following equations describe the operation of the packed tower:

1) Interphase Flux for the Dissolved Organic Component

$$\frac{d(L x_i)}{dz} = - (K_{OL} a) \, c_L \, S \, (x_i - x_i^*)$$

2) Gas-Phase Water Concentration

$$y_w = \frac{P_0}{P^*} x_w^*$$

3) Component Mass Balances

$$\frac{d(L x_i)}{dz} = \frac{d(V y_i)}{dz}$$

$$\frac{d(L x_w)}{dz} = \frac{d(V y_w)}{dz}$$

4) Enthalpy Balance

$$\frac{d[L(H_{L,i} x_i + H_{L,w} x_w)]}{dz} = \frac{d[V(H_{V,i} y_i + H_{V,w} y_w)]}{dz}$$
5) Interphase Heat Flux

\[
\frac{d[L(H_L, iX_i + H_L, wX_w)]}{dz} = \frac{d[V(H_V, iY_i + H_V, wY_w)]}{dz}
\]

6) Pressure Drop

\[
\frac{dP}{dz} = \frac{\alpha 10^6 V^2 T_V (Y_{iMW_i} + Y_{wMW_w})}{P}
\]

Auxiliary Equations

7) \( \sum x_i = 1 \)

8) \( \sum y_i = 1 \)

Use of the preceding equations as a satisfactorily complete model of the column assumes that mass transfer and heat transfer in the gas phase are unimportant. \( T_V \), the temperature of the vapor, is in reality the temperature of the interface. \( y \) is taken to be both the mole fraction of a component in the bulk gas phase and the mole fraction in the gas at the interface. This is based on the assumption that the liquid phase resistance is controlling in mass transfer. The vapor phase was assumed to be saturated at the interface conditions.

The pressure drop equation used is the correlation of Leva [1954]. Pressure drop calculations were based on data for 2-inch Pall rings. (Eckert et al., 1958)
In order to obtain a value for every variable at each element boundary nine relationships must be applied and solved for each differential element. These relationships would generally be the nine equations written in terms of the nine variables for which a solution is desired. Certain specifications involving the variables, called initial conditions or boundary conditions, may be substituted in place of one or more of the equations at certain points. However, the total number of relationships, specifications plus equations, which are applied for a differential element must equal the number of unknown variables. For the packed column the initial conditions specified at the top of the column \((z = 0, J = 1)\) are \(L, T_L, P,\) and \(x_i\). These specifications were substituted for equations \(1, 3\) (mass balance for \(H_2O\) only), \(4\) and \(6\). Although it theoretically makes no difference which of the equations is substituted for by a specification, logical choices result in convenience of the calculation.

For each differential element between the ends of the column, \(2 \leq J \leq NJ-1\), the set of nine equations shown were applied. This results in the application of the full set of nine equations \(NJ-2\) times. At the bottom of the column, \(J = NJ\), the boundary conditions specified were \(V\) and \(y_i\). These specifications were substituted for equations \(3\) (mass balance for dissolved component) and \(5\). Additionally, it was specified that \(T_V\) was equal to the saturation temperature of the vapor at bottom column pressure, replacing
In order to write and apply the equations to model the steam stripper special consideration must be given each type of equation. All equations must be linearized if not already in linear form. Algebraic equations, such as equations 2, 7 and 8, can be applied as they are written at every boundary of the differential elements. However, differential equations must be applied across the element. The equation is applied at the midpoint of the element to approximately describe the whole element. The terms involving derivatives are expressed as finite differences. This finite difference form is an approximation of the derivative. The terms involving a dependent variable are expressed as the arithmetic average of the variable at the element's boundaries.

The particular algorithm used to simultaneously solve the sets of equations describing the stripper is called BAND (Newman, 1968). This method for solving coupled ordinary differential equations involves the use of a triagonal matrix. Use of this technique places the restraint that all equations evaluated at a point must be in terms of variables located no farther than one differential element away. For example, an equation applied at a point J must be in terms of variables evaluated at J, J-1 and J+1. Since each of the differential equations is to be applied across an element, first order derivatives in these equations can be
conveniently written in terms of the variables at J and J-1 or at J and J+1. They are thus central difference equations when viewed as applying at the mid-point of the element. The order of approximation of the derivative is \( O(h^2) \), here \( O((\Delta z/2)^2) \), where \( \Delta z \) is the length of the element.

The three algebraic equations, 2, 7 and 8 were applied at each element's boundaries. The six differential equations, 1, 3, 4, 5 and 6 were applied at the mid-point of each element, and the derivatives approximated by the central difference form. All equations were expressed in terms of variables at J, or at J and J-1 or at J and J+1. All relationships expressed in variables at the same locations were grouped and solved to yield values for the variables at the element's boundaries. The total number of relationships, specifications plus equations, expressed in variables at the same location must always equal the number of dependent variables. It is seen that the relationships solved for simultaneously need not be applied at the same point in the column. The equations must only be expressed in terms of variables evaluated at the same locations in the column, J, J-1 and J+1.
Process Specification

In order to solve a set of simultaneous equations the values of a sufficient number of variables must be specified so that the number of remaining unknowns is exactly equal to the number of independent equations. The unknown variables which are assigned a value are the independent variables of the particular problem. The remaining unknowns are the dependent variables. The number of variables which must be specified will depend on the process. However, the particular variables chosen to be specified depends on the problem posed, the answers sought and the methods of analysis available.

In examining the vacuum steam stripping operation the variables of interest were identified as \( x_i, x_w, y_i, y_w, T_L, T_v, L, V \) and \( P \). These are the dependent variables. If there are \( n \) number of dissolved components then the solution to \( 2n+7 \) dependent variables is sought. \( 2n+7 \) independent equations must be solved simultaneously. To predict the performance of the column a solution for the dependent variables is needed along the length of the column. This requires that the set of independent equations be solved at points along the length of the column. The choice and number of independent variables specified and equations solved is not the same at all points in the column. Figure A-2 summarizes the choice of variables specified and the equations solved for the vacuum steam stripper. Because the
differential equations can only be applied across an element rather than at a boundary, the minimum number of specifications is equal to the number of differential equations.
Linearization

The equations can be linearized by the following technique:

1. The equations are written with all the terms on one side of the equal sign (implicit form):

   \[ f_i(T, P, L, V, x_1, \ldots, x_n, y_1, \ldots, y_n) = 0 \]

   The resulting expression is expanded with the use of Taylor's series as follows:

   \[ f_i = f_i^0 + (T-T_0) \frac{\partial f_i}{\partial T} + (P-P_0) \frac{\partial f_i}{\partial P} + (L-L_0) \frac{\partial f_i}{\partial L} \]

   \[ + (V-V_0) \frac{\partial f_i}{\partial V} \]

   \[ + (x_i-x_i^0) \frac{\partial f_i}{\partial x_i} + (y_i-y_i^0) \frac{\partial f_i}{\partial y_i} \]

   \[ + \frac{\partial P}{\partial z} \frac{\partial f_i}{\partial (dP/dz)} \]

   \[ + \frac{\partial dL}{\partial z} \frac{\partial f_i}{\partial (dL/dz)} \]

   \[ + \frac{\partial dx_i}{\partial z} \frac{\partial f_i}{\partial (dx_i/dz)} \]

   \[ + \frac{\partial dy_i}{\partial z} \frac{\partial f_i}{\partial (dy_i/dz)} \]

   The zero superscripts indicate that the variable, the function or the derivative is evaluated at some value that is initially assumed and improved after each iteration.

2. The derivatives are approximated by the use of their finite difference form. For a variable, \( Y \), which is a function of the location in the column \( Y = f(z) \), the
Taylor's series expansion around \( z_0 \) can be written as:

\[
Y(z_0 + \frac{\Delta z}{2}) = Y(z_0) + \frac{\Delta z}{2} \frac{dY(z)}{dz} \bigg|_{z=z_0} + \frac{\Delta z}{2} \frac{1}{2!} \frac{d^2Y(z)}{dz^2} \bigg|_{z=z_0} + \mathcal{O}(\Delta z^3)
\]

\[
Y(z_0 - \frac{\Delta z}{2}) = Y(z_0) - \frac{\Delta z}{2} \frac{dY(z)}{dz} \bigg|_{z=z_0} + \frac{\Delta z}{2} \frac{1}{2!} \frac{d^2Y(z)}{dz^2} \bigg|_{z=z_0} + \mathcal{O}(\Delta z^3)
\]

These equations express the value of variable \( Y \) in an interval \( \Delta z \) around \( z_0 \) (see figure A-1). The last term in each series represents the higher order terms of the expansion. These terms are neglected; therefore, the last term in the series indicates the order of magnitude of the approximation. In this case the terms neglected are of order \((\Delta z/2)^3\).

Subtracting the two series one gets:

\[
Y(z_0 + \frac{\Delta z}{2}) - Y(z_0 - \frac{\Delta z}{2}) = 2 \frac{\Delta z}{2} \frac{dY(z)}{dz} \bigg|_{z=z_0}
\]

Rearranging to express the derivative one obtains:

\[
\frac{dY(z)}{dz} \bigg|_{z=z_0} = \frac{Y(z_0 + \frac{\Delta z}{2}) - Y(z_0 - \frac{\Delta z}{2})}{\Delta z} + \mathcal{O}(\Delta z^2)
\]
Realizing that \((z_0 + \frac{\Delta z}{2}) = J\) and \((z_0 - \frac{\Delta z}{2}) = J-1\) then:

\[
\frac{dY(z)}{dz} \bigg|_{z=z_0} = \frac{Y(J) - Y(J-1)}{\Delta z} + \frac{1}{2} \left( \frac{\Delta z}{2} \right)^2
\]

This is the central difference form approximating the derivative evaluated at the midpoint of the element.

4. Adding the two series one obtains the approximation for the variable evaluated at the center of the element.
This value is the arithmetic average of the variable at the element's boundaries.

\[
Y(z_0) = \frac{(Y)J + (Y)J-1}{2} + \frac{1}{2} \left( \frac{\Delta z}{2} \right)^2
\]
Linking the Boundary Conditions to the Calculation

As was stated previously, certain specifications called initial conditions and boundary conditions are used to replace equations at certain locations. An entire set of nine relationships is needed to solve for the nine tracked variables. The specifications are employed at \( J=1 \) and \( J=N_J \). The information stated in a specification at either end of the column must be linked to an equation of the set describing the operation of the middle section of the column. A specification is linked to that equation for which the specification was substituted in the set of relationships applied at the end of the column. Specifications may be substituted for both algebraic and differential equations. However, specifications must be substituted for differential equations because differential equations must apply across an element, rather than at a boundary.

For a specification to be made in place of a differential equation at \( J=1 \) (\( z=0 \)) that equation must first be applied to the midpoint of the first element, \( z_1 \). When this equation is first applied it must be written in terms of variables evaluated at locations adjacent to the location at which the specification was made, in this case in terms of variables at \( J-1 \) and \( J \). In this way the information specified is linked to the rest of the calculation. Thus, when the equations are solved the solution provides a value
at every J boundary and no gap exists. The differential equation is applied for all elements, \(1 \leq z_0 \leq NJ-1\). In order to apply the equation for the first element the following form must be used.

\[
x(z_0) = \frac{X(J) + X(J-1)}{2}; \quad \frac{dx(z_0)}{dz} = \frac{X(J) - X(J-1)}{\Delta z}
\]

Thus central difference notation is used to link a differential equation backward to the specification at J=1. The term backward is used only in terms of the ordering of J along the length of the column. Because this form must be adopted for the first element, this form is used to apply the differential equation for all other elements. The equation will thus be used as one of the equations to solve for the variables at each J, \(2 \leq J \leq NJ\).

For a specification to be made at J=NJ (\(z=Z\)) the differential equation to which it is related would again be applied for all elements, \(1 \leq z_0 \leq NJ-1\). The equation must be expressed in the following form in order to apply the equation to the NJ-1 element.

\[
x(z_0) = \frac{X(J+1) + X(J)}{2}; \quad \frac{dx(z_0)}{dz} = \frac{X(J+1) + X(J)}{\Delta z}
\]

Thus central difference notation is used to link a differential equation forward to the specification at J=NJ. Again, because this form is required for the NJ-1 elements, this form is used to express the differential equation for
all other elements. The equation will be used as one of the equations to solve for the variables at each \( J, \)
\( 1 \leq J \leq NJ-1. \)

Additional specifications may be substituted for algebraic equations. Otherwise, algebraic equations can be written and expressed in variables evaluated at the boundary of all elements \( 1 \leq J \leq NJ. \) For differential equations, a decision must be made to express each equation in central difference form linked either backwards or forwards to a specification.

For each boundary condition specified at the top of the column, \( J=1, \) one differential equation must be written in central difference form linked forwards.

The set of nine equations are expressed as follows for each of the \( NJ-1 \) differential elements.

**Equation**

1,3(\( H_2O \)),4,6  
Central difference form linked backwards, \( NJ-1 \) times

3(solute),5  
Central difference form linked forwards, \( NJ-1 \) times

2,7,8  
Written at every element boundary, \( NJ \) times

All of the equations and specifications expressing the dependent variables at the same locations, \( J, \) \( J-1 \) and \( J+1, \) are grouped. Including equations and specifications there results \( NJ \) sets of nine relationships. Using Newman's BAND algorithm to solve the \( NJ \) relationships provides a
solution for the nine dependent variables at all NJ boundaries.
Handling of the Equations

In order to solve the equations simultaneously using the method of Newman, each equation must be linearized and expressed in terms of variables in adjacent locations.

Equation 1. Interphase Flux for Each Dissolved Component

\[ f_1 = \frac{dx_i}{dz} + x_i \frac{dL}{dz} + (K_0L) \frac{cL}{c_i} (x_i - x_i^*) = 0 \]

where

\[ x_i^* = \frac{y_i}{K_i}. \]

For an organic liquid \( K_i \) is:

\[ K_i = \frac{\gamma_i P_i}{P} \]

where, \( P_i = \exp \left[ \frac{(AP)_i}{T} + (BP)_i \right] \) and,

\[ \ln \gamma_i = \left[ \frac{A}{1 + \frac{A}{B} \frac{x_i^*}{1-x_i^*}} \right]^2 \]

(van Laar Equation)

Since \( x_i^* \ll 1 \), then \( \ln \gamma_i = A \)

At infinite dilution:

\[ \frac{d}{dT} \ln \gamma_i = \frac{dA}{dT} = - \frac{\Delta H_{\text{mix}}}{RT^2} \]

If one assumes that \( \Delta H_{\text{mix}} \) is described by the form

\[ \Delta H_{\text{mix}} = AAC + BACxT \]

in the range of temperature the packed
tower operates, one can integrate the above equation to obtain an expression for the activity coefficient. It follows that:

\[ \ln \gamma_i = A = \frac{(AAC)_i}{T} + (BAC)_i - (CAC)_i \ln T \]

Linearizing:

\[ \frac{dx_i}{dz} \bigg|_0 + (L-L^0) \frac{dx_i}{dz} \bigg|_0 + \left( \frac{dx_i}{dz} - \frac{dx_i}{dz} \right) \left( \frac{dL}{dz} \right) + \left[ x_i^0 \frac{dL}{dz} \right]_0 + \left( x_i^0 - x_i^0 \right) \frac{dL}{dz} \]

\[ + \left( \frac{dL}{dz} - \frac{dL}{dz} \right) + (K_{OL} a) C_L x_i - \frac{(K_{OL} a) C_L}{K_i} y_i^0 - (y_i - y_i^0). \]

\[ \frac{(K_{OL} a) C_L}{K_i} = (T-T^0) (K_{OL} a) C_L y_i^0 \frac{d(1/K_i)}{dT} \bigg|^{0}_{0} = 0 \]

Rearranging terms, substituting the finite-difference form of the derivatives written as central differences linked backward to the specification and substituting the variables by their arithmetic average values, one obtains:

\[ \frac{(x_i^0)_{J-1} - (x_i^0)_{J-1}}{\Delta z} \cdot \frac{L}{2} + \frac{(L^0)_{J-1} + (L^0)_{J-1}}{2} \cdot \frac{(x_i)_{J-1} - (x_i)_{J-1}}{\Delta z} \]

\[ + \frac{(L^0)_{J-1} - (L^0)_{J-1}}{\Delta z} \cdot \frac{L}{2} + \frac{(x_i)_{J-1} + (x_i)_{J-1}}{2} \cdot \frac{(x_i^0)_{J-1} + (x_i^0)_{J-1}}{2} \]
where for organic liquids:

\[
d(1/K_i) = \frac{P}{\text{EXP}[(\text{AAC}_i + \text{AP}_i)/T - \text{CAC}_i T_n + \text{BAC}_i T + \text{BP}_i]} (\frac{\text{AAC}_i + \text{AP}_i}{T^2} + \frac{\text{CAC}_i}{T})
\]

\[
= \frac{1}{K_i} (\frac{\text{AAC}_i + \text{AP}_i}{T^2} + \frac{\text{CAC}_i}{T})
\]

Equation 2. Gas Phase Water Concentration

\[
f_2 = y_w - \frac{P_w}{P} x^*_w = 0
\]

where \( P_w = \exp[\frac{(\text{AP})_w}{T} + (\text{BP})_w] \)

Since \( x^*_w \) is very small, one can safely assume that \( x^*_w = 1 \).
Linearizing:

\[ \left[ y^0_w - \frac{P_0}{P} \right] + (T - T^0) \frac{P^0}{P} \frac{(AP)^0}{T^0} + (P - P^0) \frac{P^0}{(P^0)^2} + (y^0_w - y^0_w) = 0 \]

Applying this equation at J positions:

\[ (y^0_w)^J + \frac{P^0(AP)^0}{P^0(T^0)^2} \cdot (T)^J + \frac{P^0}{(P^0)^2} (P)^J = \frac{(P^0)^2}{P^0} \left[ 2 + \frac{(AP)^0}{T^0} \right] \]

Equation 3. Mass Balance for Each Component

\[ f_3 = L \frac{dx_i}{dz} + x_i \frac{dL}{dz} + V \frac{dy_i}{dz} + y_i \frac{dv}{dz} \]

Linearizing:

\[ \left. L^0 \frac{dx_i}{dz} \right|_0 + (L-L^0) \left. \frac{dx_i}{dz} \right|_0 + \left. \left( \frac{dx_i}{dz} - \frac{dx_i}{dz} \right) \right|_0 L^0 + \left. x_i \frac{dL}{dz} \right|_0 + (x_i^0 - x_i^0) \]

\[ \left. \frac{dL}{dz} \right|_0 + \left. \frac{dL}{dz} - \frac{dL}{dz} \right|_0 x_i^0 - \left. (V-V^0) \frac{dy_i}{dz} \right|_0 - \left. v^0 \frac{dy_i}{dz} \right|_0 \]

\[ - \left. \frac{dy_i}{dz} - \frac{dy_i}{dz} \right|_0 V^0 - \left. y_i^0 \frac{dv}{dz} \right|_0 - \left. (y_i - y_i^0) \frac{dv}{dz} \right|_0 - \left. \frac{dv}{dz} - \frac{dv}{dz} \right|_0 y_i^0 \]

\[ = 0 \]

In different instances, depending on the boundary specifications, equation 3 can be written in central difference form linked either forward or backward to the
specification.

Writing in form linked backward to the specification--
After rearranging terms and substituting into the equation the finite-difference form and arithmetic average, one obtains the equation linked backwards:

\[
\frac{(x_i^0)_{J} - (x_i^0)_{J-1}}{\Delta z} \cdot \frac{(L)_{J} + (L)_{J-1}}{2} + \frac{(L^0)_{J} - (L^0)_{J-1}}{\Delta z} \cdot \frac{(x_i^0)_{J} - (x_i^0)_{J-1}}{\Delta z}
\]

\[
+ \frac{(L^0)_{J} - (L^0)_{J-1}}{\Delta z} \cdot \frac{(x_i^0)_{J} + (x_i^0)_{J-1}}{2} + \frac{(L^0)_{J} - (L^0)_{J-1}}{\Delta z} \cdot \frac{(x_i^0)_{J} + (x_i^0)_{J-1}}{2} \cdot \frac{(L)_{J} - (L)_{J-1}}{\Delta z}
\]

Writing in form linked forward to the specification--
The equation linked forward is written identically to the
equation linked backwards except that the subscript $J$ is replaced by $J+1$, and the subscript $J-1$ is replaced by $J$.

Equation 4. Enthalpy Balance

$$f_5 = \sum H_{L,i} \frac{dx_i}{dz} + L \sum x_i \frac{dH_{L,i}}{dz} + \frac{dL}{dz} \sum H_{L,i} x_i$$

$$- \nu \sum H_{V,i} \frac{dy_i}{dz} - \nu \sum y_i \frac{dH_{V,i}}{dz} - \frac{dv}{dz} \sum H_{V,i} y_i = 0$$

where: $H_L = (AL)_i + (BL)_i \cdot T$

$H_V = (AV)_i + (BV)_i \cdot T$

Linearizing and rearranging terms:

$$\left( \sum H_{L,i} \frac{dx_i}{dz} \right)^0 + \left( \sum x_i \frac{dH_{L,i}}{dz} \right)^0 \cdot L + \frac{dL}{dz} \sum H_{L,i} x_i^0$$

$$+ x_i \sum (L^0 \frac{dH_{L,i}}{dz})^0 + H_{L,i} \frac{dL}{dz}^0 + \frac{dx_i}{dz} \cdot \sum L^0 \cdot H_{L,i}$$

$$- \nu(\sum H_{V,i}^0 \frac{dy_i}{dz})^0 + \sum y_i^0 \frac{dH_{V,i}}{dz}^0 - \frac{dv}{dz} \sum H_{V,i} y_i^0$$

$$- y_i \sum (v^0 \frac{dH_{V,i}}{dz})^0 + H_{V,i} \frac{dv}{dz}^0 - \frac{dy_i}{dz} \sum v^0 \cdot H_{V,i}$$

$$+ T[ (BL)_i \sum (L^0 \frac{dx_i}{dz})^0 - (BV)_i \sum (v^0 \frac{dy_i}{dz})^0 + y_i^0 \frac{dv}{dz}^0 ]$$

$$+ \frac{dT}{dz} (\sum L^0 x_i^0 (BL)_i - \sum v^0 y_i^0 (BV)_i)$$
Again, depending on at which end a boundary condition is specified, equation 4 can be written in central difference form linked either forward or backward to the specification. The following substitutions are made to obtain the preceding equation linked backwards.

\[
T = \frac{(T)^{J+}(T)^{J-1}}{2}; \quad T^0 = \frac{(T)^0+(T)^0}{2}
\]

\[
\frac{dT}{dz} = \frac{(T)^{J-}(T)^{J-1}}{\Delta z}; \quad \frac{dT}{dz} \bigg|^{0} = \frac{(T)^{0 -}(T)^{0 J -1}}{\Delta z}
\]

and similarly for the rest of the variables.

In order to obtain equation 4 written in central difference form linked forwards the subscripts are changed; J is replaced by J+1 and J-1 is replaced by J.

Equation 5. Interphase Heat Flux

\[
f_5 = L \sum H_{L,i} \frac{dx_i}{dz} + L \sum x_i \frac{dH_{L,i}}{dz} + \frac{dL}{dz} \sum H_{L,i} x_i + h_a (T_L - T_V) = 0
\]
where: \( H_L = (A_L)_i + (B_L)_i \cdot T \)

\[ H_V = (A_V)_i + (B_V)_i \cdot T \]

Linearizing and rearranging terms:

\[
L \left[ \sum H_{L,i}^0 \frac{dx_i^0}{dz} \right] + \sum x_i^0 \frac{dH_{L,i}^0}{dz} + T_L \left[ \sum BHL_i \left( L^0 \frac{dx_i^0}{dz} \right) \right] + \frac{dL}{dz} \left| x_i^0 \right| + \sum x_i^0 \left[ L^0 \frac{dH_{L,i}^0}{dz} \right] + \frac{dL}{dz} \left| H_{L,i}^0 \right| + \sum \frac{dx_i^0}{dz} \left[ L^0 H_{L,i}^0 \right]
\]

\[
+ \frac{dT}{dz} \left[ \sum BLH_i L^0 x_i^0 \right] + \frac{dL}{dz} \left[ \sum H_{L,i}^0 x_i^0 \right] - haT_V = 2 \left[ L^0 \sum H_{L,i}^0 \frac{dx_i^0}{dz} \right] + L^0 \sum x_i^0 \frac{dH_{L,i}^0}{dz} + \frac{dL}{dz} \left| \sum H_{L,i}^0 x_i^0 \right| - \sum AHL_i \left[ L^0 \frac{dx_i^0}{dz} \right]
\]

Rearranging terms and making the following substitutions the preceding equation can be written in central difference form linked forward to the specification.

\[
T = \frac{(T)_{J+1} + (T)_J}{2}; \quad T^0 = \frac{(T)_0^0 + (T)_J^0}{2}
\]

\[
\frac{dT}{dz} = \frac{(T)_{J+1} - (T)_J}{\Delta z}; \quad \left| \frac{dT}{dz} \right| = \frac{(T)_{J+1}^0 \cdot (T)_J^0}{\Delta z}
\]

and similarly for the rest of the variables.

Equation 6. Pressure Drop
\[ f_6 = \frac{dp}{dz} - \frac{\alpha 10^6 L V^2 T}{p} \sum y_i MW_i = 0 \]

Let us define the following term to simplify the writing of the equation:

\[ U = \frac{\alpha 10^6 L^0 (V^0)^2 T^0}{p^0} \sum y_i MW_i \]

Linearizing the equation and writing in terms of backward differences one gets:

\[ \frac{(P) J - (P) J-1}{\Delta z} - \frac{U}{T^0} \cdot \frac{(T) J^+(T) J-1}{2} + \frac{U}{T^0} \cdot \frac{(P) J^+(P) J-1}{2} \]

\[ -U \cdot \beta \ln 10 \cdot \frac{(L) J^+(L) J-1}{2} - 2U \cdot \frac{(V) J^+(V) J-1}{2} \]

\[ -\frac{\alpha 10^6 L (V^0)^2 T}{p} \cdot \sum MW_i \cdot \frac{(y_i) J^+(y_i) J-1}{2} \]

\[ = -U(\beta \cdot \frac{(T)^0 J^0}{2} J-1) \cdot \ln 10 + 2) \]

Equations 7 and 8. Auxiliary Equations

There is no need to linearize the two auxiliary equations since they are already linear. Writing these equations at \( J \) positions we get:

\[ f_7 = \sum (x_i) J - 1 = 0 \]
\[ f_8 = \sum (y_i)_J - 1 = 0 \]
Ratio of Vapor Compositions

At the bottom end of the column, for the specific operating condition of zero vapor flow at that end, the ratio of the vapor mole fraction of any dissolved component to the vapor mole fraction of another component is set equal to the ratio of their rates of mass transfer at that end. Basing these ratios on the first dissolved component, one has for any given component i:

\[
\frac{y_i}{y_1} = \frac{(K_{OL_a})_i (x_i - x_i^*)}{(K_{OL_a})_1 (x_1 - x_1^*)}
\]

where:

\[
x_i^* = \frac{y_i}{K_i}
\]

\(K_i\) is defined in the same manner as in equation 1 depending on whether the dissolved materials are gases or organic substances.

Multiplying and rearranging terms:

\[
y_1y_i \cdot \left[ (K_{OL_a})_i \frac{(K_{OL_a})}{K_i} - (K_{OL_a})_1 \right] + (K_{OL_a})_1y_i x_1 - (K_{OL_a})_1 y_1 x_1 = 0
\]

Linearizing and writing the equation at the J position:

\[
(y^0_i)_J (y_i^0)_J F_2(T)_J + (K_{OL_a})_1 (y_i^0)_J (x_i)_J - (K_{OL_a})_1 (y_i^0)_J (x_i)_J
\]

\[
+ ((y_i^0)_J F_1 - (K_{OL_a})_i (x_i^0)_J \cdot (y_i)_J + ((y_i^0)_J F_1 + (K_{OL_a})_1 (x_i^0)_J)
\]

\[
\cdot (y_i)_J = -(y_i^0)_J (y_i^0)_J F_1 - (K_{OL_a})_1 (y_i^0)_J (x_i)_J + (K_{OL_a})_1 (y_i^0)_J (x_i)_J
\]
\[ + \left( y_1^0 \right)_j \left( y_1^0 \right)_j F_2 \left( T \right)_j^0 + \left[ (K_{OL}a)_1 \right] \left( x_1^0 \right)_j \left( x_1^0 \right)_j - \left( K_{OL}a \right)_i \left( y_1^0 \right)_j \]

\[ \cdot \left( x_1^0 \right)_j + \left[ (y_1^0 \right)_j F_1 - \left( K_{OL}a \right)_i \left( x_1^0 \right)_j \right] \cdot \left( y_1^0 \right)_j \]

\[ + \left[ (y_1^0 \right)_j F_1 + \left( K_{OL}a \right)_1 \left( x_1^0 \right)_j \right] \cdot \left( y_1^0 \right)_j \]

where:

\[ F_1 = \frac{(K_{OL}a)_i}{K_i^0} - \frac{(K_{OL}a)_1}{K_1^0} \]

\[ F_2 = \frac{(K_{OL}a)_1}{(K_1^0)^2} \cdot \frac{dK_1}{dT} \bigg|_{T_1^0} - \frac{(K_{OL}a)_i}{(K_i^0)^2} \cdot \frac{dK_i}{dT} \bigg|_{T_1^0} \]
Solution of the System of Equations

The system of equations at the different J positions is solved by using the subroutine "BAND" developed by Newman. (Newman, 1968). This subroutine uses 7 major arrays in which the coefficients of the unknowns and the independent terms of the equations are stored. The array "CBND" stores the values of the unknowns after calculation. The arrays "ABND", "BBND", and "DBND" store the coefficients of the unknowns at the positions J-1, J and J+1 respectively. The array "GBND" contains the independent terms of the equations at the J position.

These arrays are set up with their values in the main program for each J position, after which the subroutine "BAND" is called. Once this process is done at every J position and "BAND" is called for the last position (J=NJ), the subroutine "BAND" solves for the value of the unknowns at each J and stores the results in the array "CBND".

There are also other arrays which store the values of the unknowns at any given time, initially the starting conditions, subsequently the improved values, and finally the converged solutions.

Starting conditions.—After several trials a procedure was developed to generate a good set of starting conditions. The starting conditions vary depending on whether the operation is below or above minimum steam flow for the countercurrent process.
The general procedure outlined below was followed in setting up starting conditions.

1) All boundary conditions were matched with their specified values.

2) The temperature and the liquid flow rate throughout the column were set equal to the boundary specification of temperature and liquid flow respectively.

3) In the calculation of the countercurrent process operating with an amount of steam below the minimum steam flow, the vapor flow throughout the column was set equal to the number of moles of dissolved components in the inlet liquid. For operation above the minimum steam flow, the vapor is assumed to be the flow of steam admitted at the bottom.

4) The mole fraction of each dissolved component in the liquid phase varies linearly from top to bottom in the column. At \( J=1 \) the liquid mole fractions are set equal to the boundary conditions at this end. At the bottom of the column, \( J=NJ \), the liquid mole fractions were taken to be 1% of the entering mole fraction.

5) The vapor mole fractions at the top of the column, \( J=1 \), are estimated by assuming that complete removal of the dissolved components is achieved. It is further assumed that the vapor stream leaves the column saturated with water at the temperature of the entering liquid. This composition is assumed to remain constant throughout the column, except in the case of countercurrent steam
stripping where the mole fractions are reduced linearly to zero.

In updating the variables, a provision is made in the program to avoid negative values of the liquid and vapor mole fractions. Also, to ensure stability in the calculation there is a damper that will not allow the temperature to change by more than one degree centigrade after each iteration.

The calculation is assumed to converge when the change in the liquid mole fraction at the bottom of the column is less than one thousandth of one percent ($10^{-5}$) of the entering mole fraction. The test is applied to all dissolved components.

This level of accuracy was established after more stringent criteria ($10^{-6}$, $10^{-8}$) were tested without any effect on the results.

The number of differential sections (mesh size) in which the column was divided was decided after various mesh sizes and their effect on the results were tested. In all cases a grid with 10 mesh points per meter of column length seemed to satisfy the desired accuracy.
The Method of Newman

Many problems arise in chemical engineering which require the solution of a tridiagonal matrix.

For example, all stagewise separation processes result in equations which relate one or more variables on a given stage j to the same variables on the stage above, j+1, and to the same variables on the stage below, j-1.

A second major source of such matrices are problems in which the changes in one or more variables across a distance must be found. Such problems result in ordinary differential equations, and if more than one variable must be traced, in sets of coupled ordinary differential equations, perhaps together with algebraic equations in the same variables. The problems are boundary value problems; the variables possess certain specified values at the boundaries of the space, set by the statement of the problem to be solved.

Most of the problems encountered contain one or more non-linear equations, and then there is no direct solution. However, by means of the Newton-Raphson method, the equations can be linearized about a set of guesses for the variables at each point, and a normal iteration process followed to the converged solution.

Equations written in the unknowns at each stage or location in a mesh of points can be written in matrix form. The set of equations can be solved by simply using an algorithm for solution of a set of simultaneous equations. Such a routine could employ a Gauss-Seidel iteration
technique. However, a large number of stages or locations result in a large number of equations. Most algorithms require large amounts of computer memory and computing time to solve large numbers of equations. Because the matrix for staged or coupled equations is tridiagonal, methods can be used to solve these equations very efficiently. Such a method for solving a set of tridiagonal linear equations in one unknown variable is the Thomas method. (Lapidus, 1962). The Thomas method is a trick in which the solution to the unknown at a certain location is broken into two parts. The first part is calculated as the quotient of certain coefficients of the equation involving the unknown applied at the location of interest. The second part is the product of other coefficients of the same equation and the value of the unknown at the following location. Of course, this value is not available. However, the variable at every location can be expressed in two parts in terms of coefficients and the variable at the following location. If this is done at each location, the variable at the last location is directly calculable because no further location exists. Both parts of the solution can then be calculated for the preceding value. With this value, the next preceding value can be calculated and so on until the variable is back calculated at every location. Although the Thomas method is convenient for linear equations, the method can be applied to non-linear equations by linearization about a guess for the unknown at each position and
the set of equations can thus be solved by the method of Newton. Linearizing the equations employs a Taylor series expansion.

The method can be extended to solve for any number of unknowns at each \( j \), and it is this extension that is so valuable. The extension is due to Newman. (Newman, 1968)

Newman's subroutine for the solution of the equations is called BAND. It uses a second subroutine for matrix inversion (MATINV).

Just to see the form of the matrix that develops let us consider two unknowns at each \( j \). We now need two equations at each \( j \) of course. In order to distinguish between the unknowns, let us call them \( C \) and \( \psi \), and let us note that the coefficients of the unknowns are normally different in the two equations at \( j \) by calling them \( B \) and \( B, A \) and \( A, D \) and \( D, \) for the first unknown and the corresponding Greek symbols for the second unknown. Then the equations are

1st eq. at \( j=1 \)

\[
B_1 C_1 + \beta_1 \psi_1 + D_1 C_2 + \Delta_1 \psi_2 = G_1
\]

2nd eq. at \( j=1 \)

\[
B_1 C_1 + \beta_1 \psi_1 + D_1 C_2 + \Delta_1 \psi_2 = G_1
\]

1st eq. at \( j=2 \)

\[
A_2 C_1 + \alpha_2 \psi_1 + B_2 C_2 + \beta_2 \psi_2 + D_2 C_3 + \Delta_2 \psi_3 = G_2
\]

2nd eq. at \( j=2 \)

\[
A_2 C_1 + \alpha_2 \psi_1 + B_2 C_2 + \beta_2 \psi_2 + D_2 C_3 + \Delta_2 \psi_3 = G_2
\]
It is apparent that where we used to have a single number in the tridiagonal matrix, we now have a $2 \times 2$ matrix. In general we will have a block tridiagonal matrix which is $n \times n$, where in turn, $n$ is the number of unknowns at $j$. If we wish to solve at 100 points, $j$, for 5 unknowns, we will have to solve 100 $5 \times 5$ matrices. If we simply set up the giant matrix and solved it by Gauss-Seidel we would have to solve a $500 \times 500$ matrix, a formidable job.
Program ORGAN2

This program models the vacuum stripping of volatile, sparingly soluble organic components from water in a counter-current packed column. The program can handle up to a total of four components.

The program has the capability to break up the total number of iterations into more than one execution of the calculation. In this way the progress of the calculation can be examined at intermediate points to detect divergence. NSEC is specified by the user to be less than the total CP time. As the calculation time exceeds NSEC the program prints the results of the last iteration and punches cards containing the values of all parameters needed to continue the calculation with another execution of the program. The printed results can be examined and the calculation continued by using the punched cards as the input deck for the next execution. Table A-1 lists some of the important nomenclature used in the program. Table A-2 presents typical input data used in Program ORGAN2.
Table A-1. **Nomenclature in the program**

The following is a list of the most common parameters in the program:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Constant used in pressure drop calculation</td>
</tr>
<tr>
<td>BE</td>
<td>Constant used in pressure drop calculation</td>
</tr>
<tr>
<td>CBND</td>
<td>Array containing the value of the unknowns at every iteration. The order of the unknowns in the array is: T, L, V, x₁, ..., xᵢ, yᵢ, ..., yᵦ, p</td>
</tr>
<tr>
<td>DESCR</td>
<td>Full name of component(s) being stripped</td>
</tr>
<tr>
<td>EPS</td>
<td>Value used as the convergence criterion (usually 10⁻⁵)</td>
</tr>
<tr>
<td>HA</td>
<td>Heat transfer coefficient, Joule/s·cm³·°K</td>
</tr>
<tr>
<td>KOLA</td>
<td>Mass transfer coefficient, s⁻¹</td>
</tr>
<tr>
<td>KONT</td>
<td>If equal to zero indicates the first execution of the input data. If different from zero indicates the input data is the continuation of a previous execution.</td>
</tr>
<tr>
<td>KPRINT</td>
<td>If equal to zero, no intermediate iterations will be printed. If different from zero, all intermediate iterations will be printed</td>
</tr>
<tr>
<td>LIN</td>
<td>Liquid superficial molar-velocity at J=1, kg-mole/m²s</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NCOMP</td>
<td>Number of dissolved components</td>
</tr>
<tr>
<td>NCOMPP</td>
<td>Total number of components including water (NCOMPP=NCOMP+1)</td>
</tr>
<tr>
<td>NJ</td>
<td>Total number of J positions (NJ=NDIV+1)</td>
</tr>
<tr>
<td>NSEC</td>
<td>Number of seconds for calculation, decimal</td>
</tr>
<tr>
<td>PO</td>
<td>Column pressure at J=1, torr</td>
</tr>
<tr>
<td>PPMIN</td>
<td>Concentration of dissolved component in liquid at J=1, ppm</td>
</tr>
</tbody>
</table>
PST = Vapor pressure of water, torr
SXIN = Summation of mole fractions of dissolved components in the liquid at J=1
TAG = Abbreviated name of dissolved components(s)
TEQB = Saturation temperature of water, °K
TLIN = Liquid temperature at J=1, °C
TLINA = Liquid temperature at J=1, °K
VIN = Steam superficial molar velocity at J=NJ, kg-mole/m²s
X = Mole fraction in the liquid
XIN = Mole fraction of dissolved component in the liquid at J=1
Y = Mole fraction in the vapor phase
ZTOT = Column length, m

Constants of Equations

AAC, BAC, CAC = Activity coefficient equation
AHL, BHL = Liquid enthalpy equation
AHV, BHV = Vapor enthalpy equation
AL, BE = Pressure drop equation
AVP, BVP = Vapor pressure equation
Table A-2. Typical input data used in Program ORGANZ

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>KONT</td>
<td>0</td>
</tr>
<tr>
<td>NCOMP</td>
<td>1</td>
</tr>
<tr>
<td>NJ</td>
<td>60 boundaries</td>
</tr>
<tr>
<td>NSEC</td>
<td>15 if CP time = 20 octal seconds</td>
</tr>
<tr>
<td>KRPINT</td>
<td>0</td>
</tr>
<tr>
<td>DESCRI(I)</td>
<td>Methyl isobutyl ketone</td>
</tr>
<tr>
<td>TAG(I)</td>
<td>MIBK</td>
</tr>
<tr>
<td>MW(I)</td>
<td>100.16 kg/kgmole</td>
</tr>
<tr>
<td>KOLA</td>
<td>0.024 s</td>
</tr>
<tr>
<td>PPMIN(I)</td>
<td>15,000 ppm</td>
</tr>
<tr>
<td>AAC(I)</td>
<td>-11.732.8</td>
</tr>
<tr>
<td>BAC(I)</td>
<td>260.6</td>
</tr>
<tr>
<td>CAC(I)</td>
<td>34.344</td>
</tr>
<tr>
<td>AVP(I)</td>
<td>-5874.</td>
</tr>
<tr>
<td>BVP(I)</td>
<td>21.66</td>
</tr>
<tr>
<td>AHL(I)</td>
<td>-5418E8</td>
</tr>
<tr>
<td>BHL(I)</td>
<td>1984E6</td>
</tr>
<tr>
<td>AHV(I)</td>
<td>-5864E7</td>
</tr>
<tr>
<td>BHV(I)</td>
<td>1604E6</td>
</tr>
<tr>
<td>HA</td>
<td>0.108E7 Joules/s-cm³°K</td>
</tr>
<tr>
<td>AL</td>
<td>1541E2</td>
</tr>
<tr>
<td>BE</td>
<td>4424</td>
</tr>
<tr>
<td>PO</td>
<td>94.61 mm Hg</td>
</tr>
<tr>
<td>LIN</td>
<td>0.7442 kgmole/m² s</td>
</tr>
<tr>
<td>TLIN</td>
<td>44.8954°C</td>
</tr>
</tbody>
</table>
VIN = .01640 kgmole/m² s
ZTOT = 6 m
Input Cards

Card 1: KONT
       Format(I1)

Card 2: NCOMP,NJ,NSEC,KPRINT
       Format(20I4)

Card 3: DESCR(I),[I=1,4]
       Format(4A6)

Card 4: TAG(I),MW(I),KOLA(I),PPMIN(I)
       Format(A6,4X,5F10.0)

Card 5: AAC(I),BAC(I),CAC(I)
       Format(8F10.0)

Card 6: AVP(I),BVP(I),AHL(I),BHL(I),AHV(I),BHV(I)
       Format(8F10.0)

Card 7: HA,AL,BE
       Format(8F10.0)

Card 8: PO,LIN,TLIN,VIN,ZTOT
       Format(8F10.0)

Cards 3, 4, 5 and 6 contain data for one dissolved component. If more than one component is being considered, a set of cards for each additional component should follow the first.
PROGRAM ORGAN2 (INPUT, OUTPUT, PUNCH)
DIMENSION TAG(4), PPMIN(3), PPMOUT(3), XO(3), XIN(3), DESCR(4), K(4),
1 VD(81), NADD(81)
COMM C TL(81), TV(81), L(81), V(81), p(81), K(4,81), Y(4,81), NCOMP,
2 XG(4), Y4(4), YG(4), HLA(4), HLG(4), HVA(4), HVG(4), Z(81)
COMMON /A/ AHL(4), BHL(4)
COMMON /B/ AM(4), BM(4)
COMMON /E1/ AAC(3), BAC(3), CAC(3), KOLA(3), CL
COMMON /E2/ HA
COMMON /E3/ MW(4), AL, BE
COMMON /E4/ GBND(13), XBND(13), YBND(13)
COMMON /BND/ ABND, BBND, CBND, GBND, XBND, YBND, NU, NJ
REAL L, LIN, KOLA, LA, LG, MW, K
C******READ THE DATA
MTIME=MILSEC(DUM)
READ 1, KONT
1 FORMAT (I1)
IF (KONT.EQ.0) GO TO 6
KONT=0
READ 3, NCOMP, NCOMPP, ICTL, ICTV, ICL, ICX, ICM, ICY, ICP, NJ, NITER,
1 KONY, NU, NJ, KPRINT, NSEC
3 FORMAT (2014)
READ 4, ZTOT, HA, AL, BE, PO, LIN, TLIN, VIN, CL, TLINA
READ 4, (TL(J), TV(J), L(J), V(J), P(J), (X(I,J), I=1, NCOMP),
1 (Y(I,J), I=1, NCOMP), (Z(J), J=1, NJ)
READ 4, (XG(I), Y4(I), YG(I), HLA(I), HLG(I), HVA(I), HVG(I), Z(81)
READ 4, (AML(I), BML(I), AM(1), BML(I), AHV(I), AM(1), AVP(1), BVP(1), MW(1)),
1 I=1, NCOMP)
4 FORMAT (5E16.10)
READ 5, (TAG(I), I=1, NCOMPP)
READ 5, (DESCR(I), I=1, 4)
5 FORMAT (4/4)
GO TO 150
6 READ 3, NCOMP, NJ, NSEC, KPRINT
READ 5, (DESCR(I), I=1, 4)
DO 9 I=1, NCOMP
READ 8, TAG(I), MW(I), KOLA(I), PPMIN(I)
8 FORMAT (A6, 8(F10.0)
READ 10, AVP(I), BVP(I), CAC(I)
9 READ 10, HLA(I), HLV(I), AM(1), BML(I), AHV(I), HVG(I)
READ 10, HA, AL, BE
READ 10, PO, LIN, TLIN, VIN, ZTOT
10 FORMAT (8F10.0)
NCOMP=NCOMP+1
TAG(NCOMPP)=3MH20
AVP(NCOMPP)=-5274.29
BVP(NCOMPP)=26.855
AML(NCOMPP)=2.370E7
BHL(NCOMPP)=7.69E4
AHV(NCOMPP)=3.32E7
BHv(NCOMPP)=3.33E4
MW(NCOMPP)=16.
SPPM=0.0
SMCL=0.0
DO 11 I=1,NCOMP
XIN(I)=PPM*IN(I)/MW(I)
11 SMOL=SMOL+XIN(I)
SXIN=0.0
DO 12 I=1,NCOMP
XIN(I)=XIN(I)/(SMOL+(1.0E6-SPPM)/18.)
12 SXIN=SXIN+XIN(I)
CL=55.5
ICTL=1
ICTV=2
ICL=3
ICV=4
ICXM=ICV
ICYM=NCOMPP+ICV
ICF=2*NCOMPP+ICV+1
NU=ICP
NJ=NJ+1
DO 15 J=1,NJ
15 Z(J)=ZTOT*FLOAT(J-1)/FLOAT(NJM)
TLINA=TLIN+273.16

STARTING CONDITIONS
Y(NCOMPP,1)=EXP(AVP(NCOMPP)/TLINA+BVP(NCOMPP))/PO
IF (Y(NCOMPP,1)*GT.1.0) Y(NCOMPP,1)=1.0

DO 17 I=1,NCOMP
17 YX(NCOMPP,1)=XIN(I)/XIN(I)*Y(NCOMPP,1))
TBOTT=AVP(NCOMPP)/(ALOG(PO)-BVP(NCOMPP))
DO 19 J=1,NJ
19 TL(J)=(TBOTT-TLINA)*Z(J)/ZTOT+TLINA
TV(J)=TL(J)

P(J)=PO
L(J)=LIN
V(J)=VIN+5*LIN*SXIN
SY=0.0
SX=0.0
DO 18 I=1,NCOMP
X(I,J)=(99*(ZTOT-Z(J))/ZTOT+.01)*XIN(I)
Y(I,J)=(ZTOT-Z(J))/ZTOT*Y(I,1)
SY=SY+Y(I,J)
18 SX=SX+X(I,J)
X(NCOMPP,J)=1.-SX
19 Y(NCOMPP,J)=1.-SY

NITER=0
30 KON=0
NITER=NITER+1
DO 31 IR=1,NU
31 IR=1,NU

DO 32 IR=1,NU
32 IR=1,NU

DO 35 IC=1,NU
35 IC=1,NU

DO 35 IC=1,NU
ABND(IR, IC) = 0.0
BBND(IR, IC) = 0.0

35 DBND(IR, IC) = 0.0
IR = 1

IF (J.GT.I) GO TO 42
C..... CALCULATIONS FOR J=1 (TOP OF THE COLUMN)
DO 36 I = 1, NCOMP
BBND(IR, ICXIM+I) = 1,
GBND(IR) = XINT(I)
36 IR = IR + 1
BBND(IR, ICTL) = 1
GBND(IR) = TLINA
IR = IR + 1
BBND(IR, ICP) = 1
GBND(IR) = PO
IR = IR + 1
DO 37 I = 1, NCOMP
37 CALL E33F (I)
CALL E3SF
CALL E02
GO TO 63

42 IF (J.EQ.NJ) GO TO 49
C..... CALCULATIONS FOR INTERMEDIATE J's
DO 43 I = 1, NCOMP
43 CALL E33F (I)
CALL E3SB (NCOMPP)
CALL E04B
CALL E3SF
CALL E02
CALL EC6B
GO TO 63
C..... CALCULATIONS FOR J=NJ (BOTTOM OF THE COLUMN)
49 DO 50 I = 1, NCOMP
50 CALL E01B (I)
CALL EC3B (NCOMPP)
CALL EC4B
BBND(IR, ICV) = 1
GBND(IR) = VIN
IR = IR + 1
CALL E06B
IF (VIN.EQ.0.0) GO TO 53
51 IR = IR + 1
CALL EC02
GO TO 63
53 IF (NCOMP.EQ.1) GO TO 56
K(I) = EXP((AVP(I) + AAC(I))/TV(J) + BAC(I) - CAC(I)* ALOG(TV(J)) + BVP(I))/ +P(J)
DO 55 I=2,NCOMP
  K(I)=EXP((AVP(I)+AAC(I))*TV(J)+BAC(I)-CAC(I)*ALOG(TV(J))+BVP(I))/
  *P(J)
  FAC1=(KOLA(I)/K(I)*((AAC(I)+AVP(I))/TV(J)**2)+CAC(I)/TV(J))-
  + (KOLA(I)/K(I)*((AAC(I)+AVP(I))/TV(J)**2)+CAC(I)/TV(J))
  FAC2=KOLA(I)/K(I)-KOLA(I)/K(I)
  BBND(IR,ICTV)=Y(I,J)*Y(I,J)*FAC1/P(J)
  BBND(IR,ICP)=Y(I,J)*Y(I,J)*FAC2/P(J)
  BBND(IR,ICYM+1)=Y(I,J)*FAC2-X(I,J)*KOLA(I)
  BBND(IR,ICXM+1)=Y(I,J)*KOLA(I)
  BBND(IR,ICXM+1)=Y(I,J)*KOLA(I)
  GBNV(IR)=TV(J)*Y(I,J)*Y(I,J)*FAC1/P(J)+2.*Y(I,J)*Y(I,J)*FAC2
  1 +Y(I,J)*X(I,J)*KOLA(I)+Y(I,J)*X(I,J)*KOLA(I)

55 IR=IR+1
56 CALL EQ2

CALL EQ8
CALL BAND(J)
65 CONTINUE

C.... UPDATE THE VARIABLES
DO 66 I=1,NCOMP
  X0(I)=X(I,NJ)
DO 67 J=1,NJ
  DEL=CBND( ICTL,J)-TL(J)
  IF (ABS(DEL)GT.1.) CBND( ICTL,J)=DEL/ABS(DEL)+TL(J)
  IF (ABS(DEL)LT.1.) CBND( ICTL,J)=DEL/ABS(DEL)+TL(J)
  TL(J)=CBND( ICTL,J)
  IF (ABS(DEL)GT.1.) CBND( ICTV,J)=DEL/ABS(DEL)+TV(J)
  TV(J)=CBND( ICTV,J)
  L(J)=CBND( ICL,J)
  V0(J)=V(J)
  IF (ABS(DEL)GT.5*V(J)) CBND( ICV,J)=DEL/ABS(DEL)*5*V(J)+V(J)
  V(J)=CBND( ICV,J)
  DEL=CBND( IC, J)-P(J)
  IF (ABS(DEL)GT.10*P(J)) CBND( IPC,J)=DEL/ABS(DEL)*10*P(J)+P(J)
  P(J)=CBND( IPC,J)
DO 67 I=1,NCOMP
  IF (CBND( ICXM+1,J).GT.1.) CBND( ICXM+1,J)=(1.+X(I,J))/2.
  IF (CBND( ICXM+1,J).LT.0.0) CBND( ICXM+1,J)=X(I,J)/2.
  X(I,J)=CBND( ICXM+1,J)
  IF (CBND( ICYM+1,J).GT.1.) CBND( ICYM+1,J)=(1.+Y(I,J))/2.
  IF (CBND( ICYM+1,J).LT.0.0) CBND( ICYM+1,J)=Y(I,J)/2.
  Y(I,J)=CBND( ICYM+1,J)
67 CONTINUE

C.... CONVERGENCE CRITERION
DO 75 I=1,NCOMP
IF (ABS(X(I,NJ)-X0(I)) / XIN(I) GT 1.0E-6) GO TO 77

75 CONTINUE
    DO 76 J=1,NJM
        IF (ABS(V(J)-VO(J)) / VO(J) GT 1.0E-6) GO TO 77

76 CONTINUE
    KONV=1

77 ITTIME=MILSEC(DUM)-MTIME
    MTIME=MILSEC(DUM)
    IF (NSEC .LE. ITTIME) GO TO 78
    IF (KONV .EQ. 1) GO TO 79
    GO TO 150

78 KONT=1
    PUNCH 1,KONT,PUNCH 3,NCOMP,NCOMPP,ICTL,ICTV,ICL,ICV,ICXM,ICYM,ICP,NJ,NITER,
    1 KONV,NJ,NJM,KPRINT,NSEC
    PUNCH 4,ZTDT,MA,AL,BE,PO,LI,TLIN,VLIN,CL,TLINA
    PUNCH 4,TL(J),TV(J),L(J),P(J),(X(I,J),I=1,NCOMPP),
    1 (Y(I,J),I=1,NCOMPP),Z(J),J=1,NJ
    PUNCH 4,(XIN(I),AAC(I),BAC(I),CAC(I),KOLA(I),PPMIN(I),I=1,NCOMP)
    1 I=1,NCOMPP
    PUNCH 5,(TAG(I),I=1,NCOMPP)
    PUNCH 5,(DESCR(I),I=1,4)
    GO TO 120

C......PRINT THE RESULTS
79 PRINT 80,(DESCR(I),I=1,4)
80 FORMAT (/I6,,1X,STRIPPING OF K4A6)
    1 I=1,NCOMP
    PRINT 82,TAG(I)
82 FORMAT (/X,A6)
    PRINT 83,AHL(I),AVP(I)
83 FORMAT (/X,*VAPOR PRESSURE*,6X,*P=EXP(*,E10.4,*,/T*,E9.4,*,)*),4X,
1 *TORRE*)
    PRINT 84,AAC(I),BAC(I),CAC(I)
84 FORMAT (/X,*ACTIVITY COEFF.*,6X,*G=EXP(*,E10.4,*,/T*,E9.4,*,)*),4X,
1 *E9.4,*,*LNT(I))
    PRINT 88,AHL(I),BHL(I)
88 FORMAT (/X,*LIQUID ENTHALPY*,5X,*H=*,E10.4,*,*T*,5X,
1 *JOULES/KGMOLE*)
    PRINT 89,AHV(I),SHV(I)
89 FORMAT (/X,*VAPOR ENTHALPY*,6X,*H=*,E10.4,*,*T*,5X,
1 *JOULES/KGMOLE*)
    PRINT 90,KOLA(I)
90 FORMAT (/X,*KOLA =*,E10.4,*,/SEC*)
91 CONTINUE
    PRINT 92,PO,ZTOT
92 FORMAT (/I6,,1X,*PRESSURE =*,E10.4,* TORR*,/X,*COLUMN LENGTH =*,E10.4,
1 *M*)
    NDOT=NJ-1
    PRINT 95,NDOT
95 FORMAT (/I6,,1X,*DIVISIONS*)
96 PRINT 97,TLIN,TLIN
97 FORMAT (/I6,,1X,*LIQUID FLCW =*,E10.4,* KGMOLES/SQM SEC*,5X,
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1 *TEMP IN =*,E10.4) 
TEP=AVP(NCOMPP)/(ALOG(P(NJ))-BVP(NCOMPP))
TVINP=TEQ8-273.16
PRINT 100,VNP,TVINP

100 FORMAT (1X,*STEAM FLOW =*,E10.4,*,KGRMSLS/SMH SEC*,5X,
1 *TEMP IN =*,E10.4) 
PRINT 101,H

101 FORMAT (/1X,*HEAT TRANSFER COEFFICIENT =*,E10.4,
1 *JOULES/SEC CUM DEGK*) 
PRINT 102,AL,VE

102 FORMAT (1X,*PRESSURE DROP PARAMETERS*/SF*,*AL =*,E10.4/SF*,*BE =*,
1 E10.4) 
SM=0.0
DO 110 I=1,NCOMP
110 SMS=SMS+X(1,NJ)*MW(I)
SMS=SMS*XCOMPP,NJ)*18.
DO 112 I=1,NCOMP
112 PPMOUT(I)=X(I,NJ)*MW(I)/SM*1.0E6
PRINT 115

115 FORMAT (/1X,*PPM IN*,8X,*PPM OUT*) 
DO 117 I=1,NCOMP
117 PRINT 116,TAG(I),PPMIN(I),PPMOUT(I)
116 FORMAT (1X,A10,E10.4,5X,E10.4)
118 CONTINUE

IF (NCOMP.GT.1.OR.VIN.NE.0.0) GO TO 120
VPOUT=EXP(AVP(NCOMPP)/TV(NJ)+BVP(NCOMPP))
PICUT=PNJ->VPOUT
IF (PLOUT.LT.0.0) PICOUT=0.0
XEQ=PLOUT/EXP((AAC(I)*AVP(I))/TV(NJ)+BAC(I)-CAC(I)*ALOG(TV(NJ))+
+BVP(I))
PPMEQ=XEQ*MW(I)/(1.0E6*18.0E6)
PRINT 118,PPMEQ

118 FORMAT (1X,*PPM AT EQUIL AT OUTLET TEMP =*,E10.4)
PRINT 121,NITER
PRINT 122

122 FORMAT (1X,*ITERATION*,13)
PRINT 123

123 FORMAT (1X,*LENGTH*,4X,*LIO TEMP*,4X,*VAP TEMP*,4X,*PRESSURE*,
1 4X,*LIO FLOW*,4X,*VAP FLOW*) 
DO 125 J=1,NJ
TLPI=TL(J)-273.16
TVF=TV(J)-273.16
PRINT 123,TLPI,TVF,P(J),L(J),V(J)
125 CONTINUE

PRINT 127
PRINT 128

128 FORMAT (1X,*LIQUID AND VAPOR MOLE FRACTIONS*) 
PRINT 128,(TAG(I),I=1,NCOMP),TAG(I),I=1,NCOMP)
129 FORMAT (1X,*LENGTH*,4X,46.11(4X,A6)) 
DO 135 J=1,NJ
PRINT 130,(J),X(I,J),I=1,NCOMP),(Y(I,J),I=1,NCOMP)
130 FORMAT (1X,F6.6,8E10.4)
135 CONTINUE

IF (KONT.EQ.1) STOP
IF (KDNV.EQ.1) STOP
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150 IF (NITER.LE.5) GO TO 30
   DO 180 NT=1,5
   JMAX=2
   DMAX=ABS(TL(2)-TL(1))
   DO 155 J=3,NJ
      IF (ABS(TL(J)-TL(J-1)).LT.DMAX) GO TO 155
      JMAX=3
      DMAX=ABS(TL(J)-TL(J-1))
   CONTINUE
   JMIN=2
   DMIN=ABS(TL(2)-TL(1))+ABS(TL(3)-TL(2))
   DO 160 J=3,NJM
      IF (ABS(TL(J)-TL(J-1))+ABS(TL(J+1)-TL(J)).GT.DMIN) GO TO 160
      JMIN=J
   CONTINUE
   JMAX=JMAX+1
   155 CONTINUE
   160 CONTINUE
   IF (DMIN.GE.67*DMAX) GO TO 30
   IF (JMAX.EQ.JMIN.OR.JMAX.EQ.JMIN+1) GO TO 30
   JMAX=JMAX-1
   JMAXJMAX+1
   162 DO 165 J=JMIN,JMAX
      TL(J)=TL(J+1)
      TV(J)=TV(J+1)
      L(J)=L(J+1)
      V(J)=V(J+1)
      P(J)=P(J+1)
      Z(J)=Z(J+1)
   CONTINUE
   DO 165 I=1,NCOMPP
      X(I,J)=X(I,J+1)
      Y(I,J)=Y(I,J+1)
   165 JMAX=JMAX-1
   GO TO 172
   166 J=JMIN
   DO 170 JV=JMAXP,JMIN
      TL(J)=TL(J+1)
      TV(J)=TV(J+1)
      L(J)=L(J+1)
      V(J)=V(J+1)
      P(J)=P(J+1)
      Z(J)=Z(J+1)
   CONTINUE
   DO 170 I=1,NCOMPP
      X(I,J)=X(I,J+1)
      Y(I,J)=Y(I,J+1)
   170 J=J-1
   172 TL(JMAX)=(TL(JMAX-1)+TL(JMAX+1))/2.
   TV(JMAX)=(TV(JMAX-1)+TV(JMAX+1))/2.
   L(JMAX)=(L(JMAX-1)+L(JMAX+1))/2.
   V(JMAX)=(V(JMAX-1)+V(JMAX+1))/2.
   P(JMAX)=(P(JMAX-1)+P(JMAX+1))/2.
   Z(JMAX)=(Z(JMAX-1)+Z(JMAX+1))/2.
   DO 173 I=1,NCOMPP
      X(I,JMAX)=(X(I,JMAX-1)+X(I,JMAX+1))/2.
   CONTINUE
   GO TO 30
   END
SUBROUTINE EQIB (I)

INTERPHASE FLUX FOR DISSOLVED COMPONENT

COMMON TL(8),TV(81),IL(8),Y(81),P(81),X(4,81),Y(4,81),NCOMP,
2 XG(4),YA(4),YG(4),HLA(4),MLG(4),MVA(4),HVG(4),Z(81)

COMMON/II/ AIC(3),BAC(3),CAC(3),KOLA(3),CL

DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,27),

COMMON /BND/ ABNO,ABND,CENO,00ND,GOND,XBND,YBND,NU,NJ

REAL L,LA,LG,KOLA,KJ,KJM,LNDXR,KA

LA=(L(J)+L(J-1))/2.
LG=(L(J)-L(J-1))/DZ

IF (DZ/YA(J)/LNDXR)=ALOG(DXJ/DXJM) Go To 10

D0XD.XJO3M LNDXR=ALOG(DXJ/DXJM)
F=KOLA(I)*CL
G=*(LNDXR-DXJ)/LNDXR**2

HJ=SG*1/(-1.,KJ)

RJ=GJ*1/(-1.,KJ)

**KJM

SJ=SG*1/(KJ**P(J))

SJ=M=SG*1/(KJ**P(J-1))

ABND(IR,ICL)=RJ

ABND(IR,ICM+I)=ICM+I

BBND(IR,ICTV)=RJ

BBND(IR,ICTV)=RJ

BBND(IR,ICM+I)=HJ

BBND(IR,ICYM+I)=HJ

BBND(IR,ICP)=SGW

BBND(IR,ICP)=SJ

BBND(IR)=LA*XG(I)*XAI(1)*LG*(LNDXR-DXJ)/XJ(I,J)=GJM*XJ(I,J-1)

I +HJ*XJ(I,J-1)+RJ=TV(J)-RJ*XJ(I,J-1)+SJ*P(J)-SJ*P(J-1)

IR=IR+1

RETURN

END
SUBROUTINE E02
VAPOR PHASE CONCENTRATION OF WATER
COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMP,
  NCOMPP,ICTL,ICTV,ICL,ICV,ICXM,ICYM,ICF,IX,J,AVP(4),BVP(4),XA(4),
DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,27),
COMMON ZBND,ABND,ABBND,CEND,DBND,GBND,XBND,YBND,NJ,NJ
PST=EXP(4*AVP(NCOMPP)/TV(J)+BVP(NCOMPP))
BBND(IR,ICTV)=PST*AVP(NCOMPP)/(P(J)*TV(J)**2)
BBND(IR,ICM+NCOMPP)=1.
BBND(IR,ICP)=PST/P(J)**2
GBND(IR)=(PST/P(J)**(2.*AVP(NCOMPP)/TV(J))
IR=IR+1
RETURN
END
SUBROUTINE EQ3F (I)

C

MASS BALANCE OF DISSOLVED COMPONENT

COMMON TL(81),TV(81),L(81),V(81),X(4,81),Y(4,81),NCOMP,
1 NCOMP2,ICL,ICTV,ICL,V,ICXM,ICYM,ICZ,J,AVP(4),BPV(4),X(4,81),
2 XG(4),YA(4),YG(4),HLA(4),HLM(4),HVA(4),HV(4),Z(81)

DIMENSION ABND(13,13), BBND(13,13), CEND(13,81), DBND(13,27),
1 GBND(13), XBND(13,13), YBND(13,13)

COMMON /BND/ ABND, BBND, CBND, DBND, GBND, XBND, YBND, Nu, NJ

REAL L, LA, LG

DZ = Z(J+1) - Z(J)

LA = (L(J+1) + L(J))/2.

LG = (L(J+1) - L(J))/DZ

VA = (V(J+1) + V(J))/2.

VG = (V(J+1) - V(J))/DZ

XA(I) = (X(I,J+1) + X(I,J))/2.

XG(I) = (X(I,J+1) - X(I,J))/DZ

YA(I) = (Y(I,J+1) + Y(I,J))/2.

YG(I) = (Y(I,J+1) - Y(I,J))/DZ

BBND(IR,ICL) = XG(I)/2. + XA(I)/DZ

DBND(IR,ICL) = XG(I)/2. + XA(I)/DZ

BBND(IR,ICV) = YG(I)/2. + YA(I)/DZ

DBND(IR,ICV) = YG(I)/2. + YA(I)/DZ

BBND(IR,ICXM) = LG/2. - LA/DZ

DBND(IR,ICXM) = LG/2. - LA/DZ

BBND(IR,ICYM) = LG/2. + LA/DZ

DBND(IR,ICYM) = LG/2. + LA/DZ

GBND(IR) = LA*XG(I) + XA(I)*LG - VA*YG(I) - YA(I)*VG

RETURN

END
SUBROUTINE EQ3B (I)
C MASS BALANCE OF DISSOLVED COMPONENT
COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMP,
1 NCOMP,ICTL,ICTV,LCL,ICV,ICXM,ICYM,ICP,IJ,JAVP(4),BVE(4),X(4),
2 XG(4),YA(4),YG(4),HLA(4),HLC(4),HVA(4),HVC(4),Z(81)
DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,27),
1 GEND(13),XBNB(13,13),YBNB(13,13)
COMMON /BND/ ABND, BBND, CBND, DBND, GBND, XBNB, YBNB, NU, NJ
REAL LA, LG
DZ=Z(J)-Z(J-1)
LA=(L(J)+L(J-1))/2.
LG=(L(J)-L(J-1))/DZ
VA=(V(J)+V(J-1))/2.
VG=(V(J)-V(J-1))/DZ
XA(I)=(X(I,J)+X(I,J-1))/2.
XG(I)=(X(I,J)-X(I,J-1))/DZ
YA(I)=(Y(I,J)-Y(I,J-1))/2.
YG(I)=(Y(I,J)-Y(I,J-1))/DZ
ABND(IR,ICL)=XG(I)/2.-XA(I)/DZ
BBND(IR,ICL)=XG(I)/2.+XA(I)/DZ
ABND(IR,ICXM+I)=YG(I)/2.-VA(I)/DZ
BBND(IR,ICXM+I)=YG(I)/2.+VA(I)/DZ
ABND(IR,ICYM+I)=LG/2.-LA/DZ
BBND(IR,ICYM+I)=LG/2.+LA/DZ
ABND(IR,ICP+I)=LG/2.*VA/DZ
BBND(IR,ICP+I)=LG/2.*VA/DZ
GBND(IR)=LA*XG(I)+XA(I)*LG-VA*YG(I)-YA(I)*VG
IR=IR+1
RETURN
END
SUBROUTINE E043

ENTHALPY BALANCE

COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMPP
1 NCOMPP,ICTL,ICTV,ICL,ICV,ICXM,ICYM,ICP,ICR,IVP(4),HVPT(4),XL(4),
2 XG(4),YA(4),YG(4),HLA(4),HLG(4),HVA(4),HVG(4),Z(81)

COMMON /8/ AHV(4),BH(4)

DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,7)
1 GBND(13),XBND(13,13),YBND(13,13)

COMMON /UND/ 48ND,8BND,CND,D13ND,N0,XBN),YbND,t'4LJ,NJ

REAL L,L&,L&DZ

LA=(L(J)+L(J-1))/2.
LG=(L(J)-L(J-1))/DZ
VG=(V(J)-V(J-1))/DZ

DO 5 I=1,NCOMPP
XAl=(X(I,J)+X(I,J-1))/2.
XG(I)=X(I,J)-X(I,J-1))/DZ
YA(I)=Y(I,J)-Y(I,J-1))/DZ
YG(I)=(Y(I,J)+Y(I,J-1))/DZ
H A(I)=(HL(I,TL(J))+HL(I,TL(J-1)))/2. 
HLG(I)=(HL(I,TL(J))-HL(I,TL(J-1)))/DZ
HVG(I)=(HVI(TV(J)))-HVI(TV(J-1)))/DZ
5 CF1=CF1+(LA*XG(I)+LG*XA(I))*HL(I)/2.
12 CF2=CF2+(LA*HLA(I)+LG*HLG(I))/2.

DO 11 I=1,NCOMPP
ABND(IR,ICTL)=CF1/2.-CF2/DZ
BBND(IR,ICTL)=CF1/2.+CF2/DZ
11 CF1=CF1+HLA(I)*XG(I)+XG(I)*HLG(I)
12 CF2=CF2+HLA(I)*XG(I)+XG(I)*HLG(I)

DO 15 I=1,NCOMPP
ABND(IR,ICV)=CF1/2.-CF2/DZ
BBND(IR,ICV)=CF1/2.+CF2/DZ
15 CF1=CF1+HVA(I)*Y(I)+Y(I)*HVG(I)
15 CF2=CF2+HVA(I)*Y(I)+Y(I)*HVG(I)

DO 20 I=1,NCOMPP
ABND(IR,ICXM+1)=CF1/2.-CF2/DZ
BBND(IR,ICXM+1)=CF1/2.+CF2/DZ
20 CF1=CF1+HVA(I)*Y(I)+Y(I)*HVG(I)
22 CF2=CF2+HVA(I)*Y(I)+Y(I)*HVG(I)

RETURN
END
SUBROUTINE EQSF
HEAT TRANSFER EQUATION
COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMP,
1,NCOMP2,ICTL,ICTV,ICL,ICX,Y,ICX,Y,ICE,IR,J,AVP(4),BVP(4),XAI(4).
2 XG(4),YA(4),YG(4),HLA(4),HLG(4),HV(4),HV(4),Z(81)
COMMON /A/ AHL(4),BHL(4)
COMMON /E5/ HA
DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,27).
1 GBND(13),XBN(13,13),YBN(13,13)
COMMON /BND/ ABND, BBND, CBND, DBND, GBND, XBND, YBN, NU, AJ
REAL L,LA, LG
DZ=(J+1)-Z(J)
LA=(L(J+1)+L(J))/2.
LG=(L(J+1)-L(J))/DZ
DO 5 I=1,NCOMP
XA(I)=(XI(J,J+1)+XI(I,J))/2.
XG(I)=(XI(J,J+1)-XI(I,J))/DZ
HLA(I)=(HL(I,TL(J+1))+HL(I,TL(J)))/2.
5 HLG(I)=(HL(I,TL(J+1))-HL(I,TL(J)))/DZ
CF1=0.0
DO 10 I=1,NCOMP
CF=CF1+BHL(I)*(L*A*XG(I)+L*A*XA(I))
10 CF=CF2+BHL(I)*(L*A*XG(I)+L*A*XA(I))
CF1=CF1+HA
BBND(IR,ICTL)=CF1/2.-CF2/DZ
DBND(IR,ICTL)=CF1/2.+CF2/DZ
BBND(IR,ICTL)=HA/2.
DBND(IR,ICTL)=HA/2.
CF1=CF2=0.0
DO 12 I=1,NCOMP
CF1=CF1+HLA(I)*XG(I)+XG(I)*HLG(I)
12 CF2=CF2+HLA(I)*XG(I)
BBND(IR,ICL)=CF1/2.-CF2/DZ
DBND(IR,ICL)=CF1/2.+CF2/DZ
DO 15 1=1,NCOMP
CF1=LA*HLA(I)+L*HLA(I)
CF2=LA*HLA(I)
BBND(IR,ICX+I)=CF1/2.-CF2/DZ
15 DBND(IR,ICX+I)=CF1/2.+CF2/DZ
GBND(IR)=0.0
DO 20 1=1,NCOMP
GBND(IR)=GBND(IR)+2.*(L*AILA(I)*XG(I)+XA(I)*HLG(I))+L*HLA(I))
1 -AILA(I)*(L*AILA(I)*XG(I)+L*HLA(I))
=IR+1
RETURN
END
SUBROUTINE E068
PRESSURE DROP EQUATION
COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMP,
1 NCOMP, ICL, ICTV, ICLM, ICM, ICP, IR, J, AVP(4), BVP(4), XA(4),
2 XG(4), YA(4), YG(4), HLA(4), HLG(4), HVA(4), HVG(4), Z(81)
COMMON /SE/ MW(4), AL, BE
DIMENSION ABND(13,13), BBND(13,13), CBND(13,81), DBND(13,27),
1 GBD(13), XBD(13,13), YBD(13,13)
COMMON /BND/ ABND, BBND, CBND, DBND, GBND, XBD, YBD, NU, NJ
REAL L, LA, MW
DZ=Z(J)-Z(J-1)
TA=(TV(J)+TV(J-1))/2.
V4=(V(J)+V(J-1))/2.
PA=(P(J)+P(J-1))/2.
DO 1 I=1,NCOMP
1 YAI(I)=(Y(I,J)+Y(I,J-1))/2.
W=AL**10.*BE*LA*(VA**2)*TA*YA(NCOMP)*18./PA
DO 3 I=1,NCOMP
3 W=AL**10.*BE*LA*(VA**2)*TA*YA(I)*MW(I)/PA
ABND(IR,ICTV)=W/TA/2.
BBND(IR,ICTV)=ABND(IR,ICTV)
ABND(IR,ICL)=W*BE*ALOG(10.)/2.
BBND(IR,ICL)=ABND(IR,ICL)
ABND(IR,ICM)=W/VA
BBND(IR,ICM)=ABND(IR,ICM)
DO 7 I=1,NCOMP
7 ABND(IR,ICM+1)=AL**10.*BE*LA*(VA**2)*TA*MW(I)/PA/2.
BBND(IR,ICM+1)=ABND(IR,ICM+1)
ABND(IR,ICP)=1./DZ+W/PA/2.
BBND(IR,ICP)=1./DZ+W/PA/2.
GBND(IR)=W*(BE*ALOG(10.)*LA + 2.)
IR=IR+1
RETURN
END
SUBROUTINE EQ7

SUMMATION OF MOLE FRACTIONS IN THE LIQUID PHASE

COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMP,
1 NCOMP,ICL,ICV,ICM,ICF,IR,AVP(4),BVP(4),XA(4),
2 XG(4),YA(4),YG(4),HLA(4),HLG(4),HVA(4),HVG(4),Z(81)

DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,27),
1 GND(13),XND(13,13),YND(13,13)

COMMON ABND/ABND, BBND, CBND, DBND,GBND,XBND,YBND,NV,NJ

DO 5 IR=1,NCOMP
5 BBND(IR,ICXM+1)=1.
   GBND(IR)=1.
   IR=IR+1

RETURN
END

SUBROUTINE EQ8

SUMMATION OF MOLE FRACTIONS IN THE VAPOR PHASE

COMMON TL(81),TV(81),L(81),V(81),P(81),X(4,81),Y(4,81),NCOMP,
1 NCOMP,ICL,ICV,ICM,ICF,IR,AVP(4),BVP(4),XA(4),
2 XG(4),YA(4),YG(4),HLA(4),HLG(4),HVA(4),HVG(4),Z(81)

DIMENSION ABND(13,13),BBND(13,13),CBND(13,81),DBND(13,27),
1 GND(13),XND(13,13),YND(13,13)

COMMON ABND/ABND, BBND, CBND, DBND,GBND,XBND,YBND,NV,NJ

DO 5 IR=1,NCOMP
5 BBND(IR,ICXM+1)=1.
   GBND(IR)=1.
   IR=IR+1

RETURN
END

FUNCTION HV(I,T)

VAPOIR ENTHALPY FOR EACH COMPONENT

COMMON /B/ AHV(4),BHV(4)

HV=AHV(I)+BHV(1)*T

RETURN
END

FUNCTION HL(I,T)

LIQUID ENTHALPY FOR EACH COMPONENT

COMMON /A/ AHL(4),BHL(4)

HL=AHL(I)+BHL(1)*T

RETURN
END
SUBROUTINE BAND(J)
DIMENSION A(13,13), B(13,13), C(13,81), D(13,27), E(13,14,81), G(13)
DIMENSION X(13,13), Y(13,13)
COMMON /BND/ A, E, C, D, G, X, Y, N, NJ
101 FORMAT (15HODETERM=0 AT J=, I14)
IF (J-2) 1, 6, 8
1 NP1 = N + 1
DO 2 L = 1, N
D(I, L) = G(I)
DO 2 L = 1, N
LPN = L + N
2 D(I, LPN) = X(I, L)
CALL MATINV(N, 2 * N + 1, DETERM, B, D)
IF (DETERM) 3, 9, 4
3 PRINT 101, J
4 DD 5 K = 1, N
E(K, NP1, J) = D(K, 2 * N + 1)
DO 5 L = 1, N
E(K, L) = - D(K, L)
LPN = L + N
5 X(K, L) = - D(K, LPN)
RETURN
6 DO 7 I = 1, N
7 DO 8 J = 1, N
D(I, J) = D(I, K) + A(I, L) * X(L, K)
8 IF (J-NJ) 11, 9, 9
9 DO 10 L = 1, N
G(I) = A(I, L) + Y(I, L) * E(L, NP1, J-2)
10 IF (I-NJ) 12, 11, 12
12 DO 13 I = 1, N
D(I, NP1) = - G(I)
DO 13 L = 1, N
13 D(I, NP1) = D(I, NP1) + A(I, L) * E(L, NP1, J-1)
DO 14 K = 1, N
14 DO 15 M = 1, N
15 E(K, M, J) = - D(K, M)
IF (J-NJ) 17, 16, 17
16 DO 17 K = 1, N
C(K, J) = E(K, NP1, J)
17 IF (J-NJ) 18, 16, 16
18 DO 19 K = 1, N
C(K, M) = E(K, NP1, M)
19 DO 20 L = 1, N
20 C(K, L) = C(K, L) + X(K, L) * C(L, 3)
RETURN
END
SUBROUTINE MATINV(N,M,DETERM,B,D)
DIMENSION D(13),B(13,13),D(13,27)
DETERM= 1.0
DO 1 I=1,N
1 ID(I)= 0.0
DO 18 NN=1,N
BMAX= 0.0
DO 6 J=1,N
IF (ID(J)) 2,2,6
2 DO 5 J=1,N
IF (ID(J)) 3,3,5
3 IF (ABS(B(I,J))) BMAX) 5,5,4
4 BMAX=ABS(B(I,J))
IRCW= I
JCOL= J
5 CONTINUE
6 CONTINUE
IF (BMAX) 7,7,8
7 DETERM= 0.0
RETURN.
8 ID(JCOL)= 1
9 DO 10 J=1,N
10 B(IROW,J)= B(JCOL,J)
11 D(JCOL,K)= SAVE
12 D(IROW,K)= D(JCOL,K)
13 B(JCOL,K)= B(JCOL,K)*F
14 DO 13 J=1,N
15 F= B(I,JCOL)
16 DO 16 K=1,N
17 D(I,K)= D(I,K) - F*B(JCOL,K)
18 CONTINUE
RETURN
END
Approximate Design of Steam Stripper Using Hand Calculator

The rigorous design of the vacuum steam stripper obtained by Program ORGAN2 can be approximated. (Rasquin, 1978). For a plot of minimum steam flow versus column pressure for a given feed temperature, inlet concentration, and column length, Program ORGAN2 predicts an asymptote as the column pressure is lowered. Program ORGAN2 also predicts an asymptote as the feed temperature approaches the saturation temperature of water for a fixed column pressure, on a plot of minimum steam flow versus feed temperature. For this second plot column pressure, inlet concentration and column length are constant. Program MINSTM can be used in one of two forms to give an approximation to the asymptote value for either plot. Figure A-3 is an example of such a plot. Program MINSTM predicts a false minimum for each of the above plots, and this predicted minimum gives an approximation to the asymptotic value of steam flow predicted by the rigorous calculation. The approximate value of steam flow is always greater than the value obtained rigorously. This is due to the approximation in Program MINSTM that all of the steam flows to the top of the column before any of it condenses. The estimated value is only about 15% more than the true value. Using this value results in a conservative design. Program MINSTM is well suited to be programmed on a hand calculator.
**Program MINSTM**

Program MINSTM approximates the performance of a steam stripper. The calculation can be used for either a fixed column pressure or fixed feed temperature. In either case the calculation is performed to predict column pressure drop, outlet temperature, and required steam flow. The calculation is performed across a range of values for the unfixed variable. The minimum value of steam flow across the range of the unfixed variable approximates the asymptotic value calculated rigorously. Program MINSTM uses the same nomenclature as Program ORGAN2.
Input Cards

Card 1: NCOMP, EPS, AL, BE, LINMA, Z, CPPMM
       Format(I2,8X,6F10.0)

Card 2: AVP(TCOMP), BVP(TCOMP), AHL(TCOMP), BHL(TCOMP),
       AHV(TCOMP), BHV(TCOMP)
       Format(6F10.0)

Card 3: DESCR(I)
       Format(4A6)

Card 4: TAG(I), MW(I), PPMIN(I)
       Format(A6,4X,2F10.0)

Card 5: AVP(I), BVP(I), AHL(I), BHL(I), AHV(I), BHV(I)
       Format(6F10.0)

Card 2 is for the input of the properties of water.
Cards 4 and 5 must be repeated for each dissolved component.

EPS = Convergence criteria for pressure drop iteration

LINMA = Feed stream mass velocity in lb per unit time per unit cross section of empty tower

CPPMM = Top column pressure in mm of Hg
Form of Program MINSTM in Which T is the Unfixed Variable

```
PROGRAM MINSTM (INPUT,OUTPUT)
DIMENSION TAG(4),NUN(3),PPMIN(3),DESCRI(4),PST(4),AVP(4),BVP(4),
        XIN(3),MIN(3)
CVM,CVM/CL,CVM/SHL(4),BHL(4)
INTEGER TCMP
REAL L,IN,M,FMIN,FMIN
READ 1,NCOMP,PSAL,NCMP,DESCRI(2),CPV
1 FORMAT (12,5F10.0)
TCMP=NCOMP+1
READ 2,AVP(TCMP),BVP(TCLKP),AHL(TCMP),BHL(TCMP),AHV(TCMP),
        BHV(TCMP)
2 FORMAT (CP1,U0)
TLIN=AVP(TCMP)/(ALUG(CPMX)-BVP(TCMP))
TIN=TLIN-273.16
TAG(TCMP)=3H2U
READ 3,(DESCRI(I),I=1,4)
3 FORMAT (AG)
DC 5 I=1,NCOMP
FLAG,NUN(1),PPMIN(1)
* FORMAT (AG,*X,3F10.0)
5 READ 6,AVP(1),BVP(1),AHL(1),SHL(1),AHV(1),BHV(1)
6 FORMAT(DF10.0)
PRINT 7,(DESCRI(I),I=1,4),PPMIN(1)
7 FORMAT(1H1,*ESTIATION OF THE MINIMUM STEAM FLOW/
+1X,*GAS SOLVED COMPONENT = *,EAG/
+1X,*INLET CONCENTRATION = *,F7.4,* PPM*/
PRINT 5,AHL(1),BHV(1)
8 FORMAT(7A,6A17,5X,SM=M,E10.4,**,E9.4,T*,5X,
+*JULES/KGULE*)
PRINT 7,AHL(1),BHV(1)
9 FORMAT (1X,*LiqC ENTHALPY*,6X,*H=M,E10.4,**,E9.4,T*,5X,
+*JULES/KGULE*)
SPPM=0.0
SMCL=0.0
DC 11 I=1,NCOMP
PMIN(1)=PPMIN(1)/4M(1)
SPPM=SPPM+PMIN(1)
11 SMC=SML+PMIN(1)
XIN=3.0
DC 12 I=1,NCOMP
XIN(I)=MIN(I)/(SML+(1.024-SPPM)/16).
12 SINC=XIN*XIN
AVW=0.0
DC 13 I=1,NCOMP
13 AVW=AVW+XIN(I)*MIN(I)
AVW=AVW+(1.0-SXIN)3/16.
14 XIN=1.0X/((1.04)**2)*2600.0232*AVW)
OPL=OPL+30.0
DC 16 I=1,NCOMP
16 OPL=OPL+XIN(I)*(HV(I)-H-(I,TIN))+CVAP
PRINT 20,LIN,TIN,OPL
```

IF (TLIN.LT.(TSAT/1.1)) GO TO 21

TEQB = VP(TCOMP)/(ALCG(PC)-BVP(TCMF))

PST(TCOMP) = EXP(VP(TCOMP)/TLIN+BVP(TCMF))

PNJ = PC

YH2O = S1(TCOMP)/PD

AVMV = YH20 * 1.8

CVAP = 0.0

DO 15 I = 1,NCOMP

QVAP = LTNX(INI I) * (HV(I,TLIN)-HL(I,TLIN)) - QVAP

15 AVMWV = AVMWV * (1.0-YH2O)*M(I)*XIN(I)/XIN

AVMWV = (18.0+AVMWV)/2.

IT = 0

SI = LIN*XIN*YH20/(1.0-YH20)

TEO3 = AVP(TCOMP)/1. ALG1(PNJ) = BVP(TCOMP)

POLD = PNJ

OHT = LIN*(1.0-XIN)*(HL(TCOMP,TEQB)-HL(TCOMP,TLIN))

HVAP = HV(TCOMP,TEQB)-HL(TCOMP,TEQB)

SMIN = QVAP+OHT)/HVAP+SI

DEL = ALG*BE*LIN)*SMIN**2*AVMWV*TEQB*Z

P NJ = (PC+SQRT(PD**2+4.*DEL))/2.

IT = IT+1

IF (IT.GE. 40) GO TO 10

IF (ABS(POLD-PNJ)/PCLD.GT.EPS) GC TC 17

SM = SMIN/LIN

G1 = S1*HVAP

TCLT = TEQB-273.16

TI = TLIN-273.16

PRINT 18,TIN,TOUT,PNJ,SMIN,SM,P, HVAP,QVAP,S1,G1,OHT

18 FORMAT(1X,2(F7.3,2X),F7.2,2X,E5.4,2X,E5.4,5(2X,E5.4))
Form of Program MINSTM in Which P is the Unfixed Variable

```fortran
PROGRAM MINSTM (INPUT,OUTPUT)
DIMENSION TAG(4),MW(3),PPMIN(3),DESCR(4),PST(4),AVP(4),BVP(4),
XIN(3),M Vict(3),
COMMON/CL/AHL(4),BHL(4)
COMMON/CV/AHV(4),BHV(4)
INTEGER TCOMP
REAL LINMA,LIN,MW,MMIN,MSMIN
DATA 1,NCOMP,EPS,AL,LE,LINMA,Z,CPMM
1 FORMAT(12,6X,GF10.0)
TCOMP=NCOMP+1
READ 2,AVP(TCOMP),BVP(TCOMP),AHL(TCOMP),BHL(TCOMP),AHV(TCOMP),
+BVH(TCOMP)
2 FORMAT(GF10.0)
LIN=AVP(TCOMP)/(ALOG(CPMM)-BVP(TCOMP))
TIN=LIN-273.16
TAG(TCOMP)=3H2O
READ 3,DESCR(I),I=1,4
3 FORMAT (4AD)
DO 5 I=1,NCOMP
READ 4,TAG(I),MW(I),PPMIN(I)
5 FORMAT (6F10.0)
PRINT 7,DESCR(I),I=1,4,PPMIN(I)
7 FORMAT(1HI,ESTIMATION OF THE MINIMUM STEAM FLUX//
+1X,*DISSOLVED COMPONENT = *,4AD/
+1X,*INLET CONCENTRATION = *,F7.0,* PPM/*)
PRINT 3,AHL(I),BHL(I)
6 FORMAT(1A,ELIQUID ENTHALPY*,5X,*H=*,E10.4,***,E9.4,*T*,5X,
+Jcules/kgmole=*,SPFM=0.0
+AVW(L).0
DC 11 I=1,NCCMP
MMIN(I)=PPMIN(I)/MW(I)
SPFM=SPFM+PPMIN(I)
11 MXL=SMOL+MMIN(I)
SXIN=0.0
DC 12 I=1,NCCMP
XIN(I)=MIN(I)/(SMOL+((1.0E6-SPPM)/ 18.))
12 SXIN=SXIN+XIN(I)
AVW=0.0
DC 13 I=1,NCCMP
13 AVMWL=AVWWL*XIN(I)*MM(I)
AVMWL=AVMWL+(1.-SXIN)*18.
LIN=LINMA/(1.*3046**2)*3600.*2.2046*AVMWL)
QVAP=0.0
DC 16 I=1,NCOMP
16 QVAP=LIN*XIN(I)*(HV(I,TLIN)-HL(I,TLIN))+QVAP
PRINT 25,LIN,TIN,QVAP
```

108.
109.

```plaintext
PRINT 10,1X,LENGTH*,4X,TGT*,3X,TCP*,3X,P(*BOT),7X,SMIN*,
+5X,SMIN/L*,7X,HVAP*,9X,S1*,9X,Q1*,8X,QH*,
P0=CPMM
SMIN=0.0
14 PC=PO+(CPMM*,.01)
IF(P0>.3*(CPMM*+.4))GO TO 21
TEOB=AV(TCOMP)/(ALOG(PC)—2VP(TCOMP))
PF=EXP(AVP(TCCMP)/TLIN+EVP(TCCMP))
PF=PF
YH20=3T(TCOMP)/PD
AV1=AVY=YM20=18
DC 15 I=1,NCCMP
15 AVM=AVMWV+(1—YH2C)*MK(I)*XIN/I)/SNIN
AVMWV=(I8,AVMWV)/2.
I=I0
S1=LIN/SXIN*YH20/(1—YH20)
MCAL=0
17 TE0=TAV(TCOMP)/*(ALOG(PNJ) —EVP(TCOMP))
PCL=PNJ
QH=LIN*(1—SNIN)*((L(TCCMP,TEOB)—L(TCCMP,TLIN))
HVAP=HV(TCCMP,TEOB)—L(TCCMP,TECB)
IF(MCAL.GT.0)GO TO 175
SMIN=(QVAP+QHT)/HVAP+S1
175 DEL=(AL#10,5E6$=LIN)*SMIN**2*AVMWV*TEOB*Z
PF=(EF+SORT(PG**2+4*DEL))/.2.
I=I+1
IF(I0.3E.40)GO TO 19
IF(ABS(PNJ-PNJ)/PCL*GT.0)GO TO 17
I0=I0*TEOB—273.16
IF(ABS(GNNT-MIN) .GE.0.0)'SMIN=MN
GO TO 14
19 PRINT 20
20 FORMAT(1X,*NUMBER OF ITERATIONS EXCEEDED 40 *)
GO TO 14
21 CONTINUE
PRINT 24
SMIN=SMIN
PC=CPMM
PNJ=CPMM*(CPMM*1)
IF(MCAL.GT.0)GO TO 21
GO TO 17
24 FORMAT(1H—)
25 FORMAT(1X,*LIM = *,F6.4,2X,*TIN = *,F7.3,2X,*QVAP = *,E9.4)
26 CONTINUE
01=(SMIN—HVAP)—QVAP—QHT
S1=QV/HVAP
PRINT 10,2,TGT,PO,PNJ,SMIN,SPW,HVAP,S1,Q1,QHT
END
```
FUNCTION HV(12,12)
CALL CV/AVH(4),BH
HV=HV(12)+BH(12)*T2
RETURN
END

FUNCTION HL(11,11)
CALL CV/CL/AHL(4),BHL(4)
HL=HL(11)+BHL(11)*T1
RETURN
END
Appendix B

Extractor Calculation Procedure
The first step in finding the equations governing an operation is to identify the variables of interest. For the design of the extractor it was desired to specify the total number of equilibrium stages and the input mass flow-rates. The variables to be tracked were decided to be $L$, $V$, all $x$'s and all $y$'s for every stage. For only one dissolved component in the feed stream this results in a total of six dependent variables for each stage: an inter-stage flow and three compositions for each phase. Because extraction is isothermal and pressure drop is not important $T$ and $P$ are not required to be tracked at each stage.

Figure B-1 represents a useful way to number the streams and stages. The six equations relating the six variables and describing the extraction operation are as follows:

1) Equilibrium equations

\[ K_i = \frac{y_i}{x_i} \]

2) \[ \sum y_i - \sum x_i = 0 \]

3) Material balance around each stage

\[ L(M) + V(M + 1) = L(M + 1) + V(M) \]

The above equation can be solved simultaneously using Newman's BAND if desired. However, stagewise calculations without reflux and reboilers are well suited to be solved
with a relaxation technique. A set of interstage flows and stage compositions is first assumed. Each stage is considered and calculated singly. The errors in heat and/or mass balance for the stage are calculated, and new estimates of the flows and conditions for the stage are made in order to reduce or relax the errors to zero. When this has been done for one stage, then the calculation proceeds to the next stage. Although relaxation methods are highly stable, they converge slowly unless the system does not reflect errors back into the calculation with recycle streams. For asymptotic solutions relaxation methods are subject to creep and the use of multivariate Newton-Raphson schemes may be effective as the final solution is approached.

To employ the relaxation method to extraction it is useful to combine the inlet streams to each stage into one feed stream. For the internal calculation of each stage, \( F \) is defined as the combined mass flowrate and \( z_i \) is defined as the mass fraction in the feed stream. Figure B-2 shows the nomenclature employed for the calculation of one stage. Using component mass balances, Equation 2 can be shown to be equivalent to the following function.

\[
\sum y_i - \sum x_i = \sum \frac{z_i(K_i - 1)}{V/F(K_i - 1) + 1} = 0
\]

Other functions can be shown to equal equation 2 but the given function is preferred. One advantage is that the
function is monotonic and, therefore, will not converge to spurious roots. Another advantage is that the value of the flow distribution in the stage, V/F, is bounded between one and zero. Each stage can be solved using the equations and forcing the function to zero. The calculation is, in effect, a succession of flashes of the liquid feed. The calculation is reiterated using the newly calculated flows and compositions as the feed to each stage. The solution is achieved when the flows and compositions do not change more than a specified amount between iterations.
Program EXTRACT

Program EXTRACT calculates the outlet flows and compositions of a countercurrent extractor. The number of theoretical stages and the flows and compositions of inlet streams are specified by the user. The program employs a relaxation method to flash the combined feed to each stage into two liquid phases. In this way the distribution of each component is calculated to give the composition of each stream leaving the stage. The calculation of each stage is converged around the value of the flow distribution, V/F, for that stage. The solution is reached when the change of component flows in the outlet streams do not change by more than a specified fraction between iterations.

The program is capable of handling up to seven components in the system. Table B-1 lists some of the more important nomenclature used in Program EXTRACT. Table B-2 gives typical input data used in Program EXTRACT.
Table B-1. Nomenclature used in Program EXTRACT

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Number of stages specified</td>
</tr>
<tr>
<td>K</td>
<td>Total number of components</td>
</tr>
<tr>
<td>J</td>
<td>Number of components used to correlate distribution coefficient with mass fraction in phase 2</td>
</tr>
<tr>
<td>M</td>
<td>Stage number, ( M \leq N )</td>
</tr>
<tr>
<td>L(M)</td>
<td>Total mass flowrate of phase 1 for each stage</td>
</tr>
<tr>
<td>V(M)</td>
<td>Total mass flowrate of phase 2 for each stage</td>
</tr>
<tr>
<td>F(M)</td>
<td>Total mass flowrate of both phases fed to each stage</td>
</tr>
<tr>
<td>X(M,I)</td>
<td>Component mass fraction in phase 1 for each stage</td>
</tr>
<tr>
<td>Y(M,I)</td>
<td>Component mass fraction in phase 2 for each stage</td>
</tr>
<tr>
<td>Z(M,I)</td>
<td>Component mass fraction of combined feed stream for each stage</td>
</tr>
<tr>
<td>KW(M,I)</td>
<td>Distribution coefficient (weight) of component between phases 2 and 1, i.e., ( KW(M,K) = Y(M,K)/X(M,K) )</td>
</tr>
<tr>
<td>AK(I)</td>
<td>Parameters used in function to correlate distribution coefficient and mass fraction in phase 2, i.e., ( KW(M,K) = [(AK(K)*(Y(M,J)**2.0)) + (BK(K)*Y(M,J))+CK(K)] )</td>
</tr>
<tr>
<td>BK(I)</td>
<td></td>
</tr>
<tr>
<td>CK(I)</td>
<td></td>
</tr>
<tr>
<td>VOF(M)</td>
<td>Distribution of phases leaving each stage</td>
</tr>
<tr>
<td>FNC</td>
<td>Function forced to zero in order to converge value of VOF(M) by Newton method</td>
</tr>
<tr>
<td>EPSF</td>
<td>Convergence criteria: absolute error allowed in VOF(M) calc.; Newton method</td>
</tr>
<tr>
<td>EPST</td>
<td>Convergence criteria: fraction of change allowed in component flows between successive iterations</td>
</tr>
<tr>
<td>CFL(M)</td>
<td>Stored value of component mass flowrate in phase 1 leaving Nth stage from previous iteration</td>
</tr>
</tbody>
</table>
CFV(M) = Stored value of component mass flowrate in phase 2 leaving 1st stage from previous iteration

ERRL = Amount of change in component mass flowrate in phase 1 leaving Nth stage between successive iterations

ERRV = Amount of change in component mass flowrate in phase 2 leaving 1st stage between successive iterations
Table B-2. Typical input data used in Program EXTRACT

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>K</th>
<th>J</th>
<th>EPSF</th>
<th>EPST</th>
<th>L(1)</th>
<th>X(1,1) = X(1,4) = X(1,5) = X(1,6) = X(1,7) = 0.0</th>
<th>X(1,2)</th>
<th>X(1,3)</th>
<th>V(N+1) = 5.7 lbs/hr</th>
<th>Y(N+1,1) = 1.0</th>
<th>Y(N+1,2) = Y(N+1,3) = Y(N+1,4) = Y(N+1,5) = Y(N+1,6) = Y(N+1,7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>= 6 stages</td>
<td>= 3 components</td>
<td>= 3 components</td>
<td>= .000001</td>
<td>= .000</td>
<td>= 100. lbs/hr</td>
<td></td>
<td>= .995</td>
<td>= .005</td>
<td></td>
<td>= 1.0</td>
<td></td>
</tr>
</tbody>
</table>

For system at 50°C,

<table>
<thead>
<tr>
<th>AK(LL)</th>
<th>BK(LL)</th>
<th>CK(LL)</th>
<th>CNAME(LL)</th>
<th>NCOMP(LL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.60574</td>
<td>4.2047</td>
<td>MIBK</td>
<td>1</td>
</tr>
<tr>
<td>0.0</td>
<td>0.24444</td>
<td>-3.6980</td>
<td>PHENOL</td>
<td>2</td>
</tr>
<tr>
<td>20.5968</td>
<td>-9.5562</td>
<td>4.6983</td>
<td>H₂O</td>
<td>3</td>
</tr>
</tbody>
</table>
**Input Cards**

Card 1: \( N, K, J, EPSF, EPST \)  
Format (3I3, 1X, 2F10.0)

Card 2: \( L(1), X(1,1), X(1,2), X(1,3), X(1,4), X(1,5), X(1,6), X(1,7) \)  
Format (8F10.0)

Card 3: \( V(N+1), Y(N+1,1), Y(N+1,2), Y(N+1,3), Y(N+1,4), Y(N+1,5), Y(N+1,6), Y(N+1,7) \)  
Format (8F10.0)

Card 4: \( AK(LL), BK(LL), CK(LL), CNAME(LL), NCOMP(LL) \)

Card 4 is repeated for each component in the system.
PROGRAM EXTRACT(INPUT, OUTPUT)

* THIS PROGRAM CALCULATES THE OUTLET FLOWS AND COMPOSITIONS OF A
* COUNTERCURRENT EXTRACTOR. THE NUMBER OF THEORETICAL STAGES AND
* THE FLOWS AND COMPOSITIONS OF INLET STREAMS MUST BE SPECIFIED
* BY THE USER. THE PROGRAM CAN HANDLE UP TO SEVEN COMPONENTS

REAL L(21), KW(21, 7)

DIMENSION V(21), F(21), VOF(21), AK(7), BL(7), CK(7), FZ(21, 7), X(21, 7),
+Y(21, 7), Z(21, 7), NCOMP(7), CNAME(10), CFL(7), CFV(7)

READ INPUT DATA

READ 10, N, K, J, EPSF, EPSL

10 FORMAT(3I3, 1X, 2F10.0)

READ 11, L(1), X(1,1), X(1,2), X(1,3), X(1,4), X(1,5), X(1,6), X(1,7)

READ 11, V(N+1), Y(N+1,1), Y(N+1,2), Y(N+1,3), Y(N+1,4), Y(N+1,5),
+Y(N+1,6), Y(N+1,7)

11 FORMAT(8F10.0)

DO 13 L=1, K

13 CONTINUE

IT=0
SY=1.0
SX=1.0

ESTABLISH ESTIMATES FOR INTERSTAGE FLOWS, STAGE FLOW DISTRIBUTION
AND STAGE COMPOSITIONS

DC 14 LA=1, N
L(LA+1)=L(1)
V(LA)=V(N+1)
VOF(LA)=.5

DC 14 LB=1, K
X(LA+1, LB)=X(1, LB)
Y(LA, LB)=Y(N+1, LB)

14 CONTINUE

DC 1 LL=1, K
CFI( LL)=L(N+1)X(N+1, LL)
CFV( LL)=V(1)Y(1, LL)

1 CONTINUE

BEGINNING OF LOOP FOR STAGE FLASH CALCULATIONS

CALCULATE STAGE FEED FLOW AND COMPOSITIONS - NORMALIZE WT FRACTION

2 DC 8 M=1, N
F(M)=L(M)*V(M+1)

DC 3 LC=1, K
FZ( , LC)=L(M)*X(M, LC)+V( M+1)*Y(M+1, LC)
Z( , LC)=FZ(V, LC)/F(M)
Y(M, LC)=Y(M, LC)/SY
X(Y+1, LC)=X(M+1, LC)/SX

3 CONTINUE
CALCULATE DISTRIBUTION COEFF. FOR EACH COMPONENT FOR NEXT FLASH
CALCULATION BASED ON LAST ITERATION ORGANIC PHASE COMPOSITION

DO 4 LD=1,K
KW(M,LD)=EXP((AK(LD)*(Y(M,J)*2.0)+(BK(LD)*Y(N,J))+CK(LD))
4 CONTINUE

FNC=C,C
DERIV=0.0

PERFORM FLASH CALCULATION & CONVERGE VALUE OF VOF W/ NEWTON METHOD
GENERATE NEW VALUES FOR VOF,L,V,X,Y

DO 6 LE=1,K
DENY=VOF*(KW*(LE)-1.0)+1.0
FNC=FNC+((Z*(LE)*(KW(LE)-1.0))/DENY)
DE=IV=DERIV*-(Z*(LE)*(KW*LE)-1.0)**2 / (DENY)**2 )
6 CONTINUE
IF(((ABS(FNC)).LE.EPSF) GO TO 7
VOF(M)=VOF(M)-(FNC/DERIV)
GO TO 5

V(X)=F(M)-VOF(M)
L(N+1)=F(M)-V(M)
SY=0.0
SX=0.0
DO 8 LF=1,L
Y(M,LF)=(Z*(LF)*KW(P,LF))/((VOF(M)*(KW(N,LF)-1.0)+1.0)
X(N+1,LF)=Y(K,LF)/KW(M,LF)
SY=SY+Y(M,LF)
SX=SX+X(M+1,LF)
8 CONTINUE
END OF LOOP FOR STAGE FLASH CALCULATION

CONTINUE
IT=IT+1
DO 9 LS=1,K
ERRV=AGS(V(1)+Y(1,LF)-CFV(LG))
IF (ERRV. GT. (CFV(LG)*EPST)) FLG=1.0
CFL=AGS(L(N+1),X(N+1,LF)-CFL(LG))
IF (ERRV. GT. (CFL(LG)*EPST)) FLG=1.0
CFV(LG)=L(V+1)+X(N+1,LF)
CFV(LG)=V(1)+Y(1,LF)
9 CONTINUE
IF (FLG.LE.200) GO TO 100
FLC=0.0
IF (IT.LE.20) GO TO 2
C PRINT OUTPUT VALUES

C

PRINT 59
59 FORMAT(1X,*SOLUTION DID NOT CONVERGE IN 20 ITERATIONS*)

100 PRINT 110
110 FORMAT(5X,*CALCULATION OF COUNTERCURRENT EQUILIBRIUM STAGE *),
+*EXTRACTOR*).
PRINT 120,N

120 FORMAT(1HO,15X,*NUMBER OF EQUILIBRIUM STAGES =*,I3)
NP=N+1
PRINT 130,NP,NP

130 FORMAT(1HO,15X,*STREAM* ,L1(*,12,X),11X,*L(1) ,11X,*V(1) ,11X,*L(*,12,X),11X,
+*V(*,12,X))
PRINT 140,L(1),V(1),L(N+1),V(N+1)

140 FORMAT(17X,*TOTAL FLOW* ,5X,2(F6.2,X,F6.2,T0X))
PRINT 150

150 FORMAT(17X,*WEIGHT FRACTION*)
DD 170 LH=1,K
PRINT 160,CNAME(LH),X(1,LH),Y(1,LH),X(N+1,LH),Y(N+1,LH)
160 FORMAT(20X,A10,5X,4(1PE10.3,5X))

170 CONTINUE
EPSTP=EPSTP*100.
PRINT 180,IT,EPSTP

180 FORMAT(1HO,15X,*SOLUTION REQUIRED * ,I2,* ITERATIONS FOR COMPONENT* 
*: FLOWS TO CONVERGE TO WITHIN * ,F6.4,* PERCENT*)
STCP
END
Appendix C

Calculation and Discussion of Physical Properties Used in The Calculation of the Vacuum Steam Stripper
Introduction

Activity coefficients for MIBK in water were required to represent the vapor-liquid equilibrium of the binary system under study.

Mutual solubility data of the organic component and water were used to obtain the values of the activity coefficient at a given temperature. The activity coefficient of the organic solute was estimated at temperatures other than the temperatures at which the experimental data was available. This was done by calculating the constants of the activity coefficient equation at the temperatures where the solubility was known, and interpolating their values to the desired temperatures.

Initially, the two-suffix Margules equation (one constant) was used to correlate the solubility data of the organic component, but unsatisfactory results were obtained. Brian [1965] tried three models to represent activity coefficients from liquid phase solubilities and found that the van Laar equation gave the most reasonable predictions across composition for several non-ideal binary systems.

The calculations, then, used the van Laar equation together with equations expressing the liquid-liquid equilibrium between the organic and the aqueous phases. The equations are linearized as shown in Appendix A and the resulting set of equations solved by the Gauss elimination method.
Activity Coefficient

The following calculation predicts activity coefficients at a given temperature for a dissolved organic solute in water from mutual solubility data at the same temperature. The equations used are the following:

Equilibrium between the organic phase and the aqueous phase for each component

1) \( \gamma_i^0 (1 - x_i^0_w) = \gamma_i^a x_i^a \)

2) \( \gamma_w^0 x_w^0 = \gamma_w^a (1 - x_i^a) \)

Activity coefficient equations

3) \( \gamma_i^a = \exp \left( \frac{A}{1 + \frac{A}{B} \cdot \frac{x_i^a}{1 - x_i^a}} \right)^2 \)

4) \( \gamma_w^a = \exp \left( \frac{B}{1 + \frac{B}{A} \cdot \frac{1 - x_i^a}{x_i^a}} \right)^2 \)
5) \( \gamma_i^0 = \exp \frac{A}{1 + \frac{A}{B} \cdot \frac{1-x_i^0}{x_i^a}} \)

6) \( \gamma_w^0 = \exp \frac{B}{1 + \frac{B}{A} \cdot \frac{x_w^0}{1-x_w^0}} \)

Superscripts indicate the liquid phase (0 = organic, a = aqueous) and subscripts indicate the component (i = organic solute, w = water).

The unknowns are the two constants of the van Laar equation and all four activity coefficients. The results of the calculation are listed in table C-1 along with empirical expressions fit to predict activity coefficients over a range of temperature.
Table C-1. Values of Solubility and Activity Coefficients at Various Temperatures

<table>
<thead>
<tr>
<th>(x_m \times 10^2)</th>
<th>(x_w^0)</th>
<th>(A)</th>
<th>(B)</th>
<th>(\gamma_m^0)</th>
<th>(\gamma_w^0)</th>
<th>(\gamma_m^a)</th>
<th>(\gamma_w^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIBK</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30°C</td>
<td>.3324</td>
<td>.1038</td>
<td>5.6960</td>
<td>2.4980</td>
<td>1.1034</td>
<td>9.6055</td>
<td>273.23</td>
</tr>
<tr>
<td>50°C</td>
<td>.2651</td>
<td>.1222</td>
<td>5.8970</td>
<td>2.3376</td>
<td>1.0163</td>
<td>8.1614</td>
<td>336.55</td>
</tr>
<tr>
<td>75°C</td>
<td>.2485</td>
<td>.1400</td>
<td>5.9449</td>
<td>2.2084</td>
<td>1.0195</td>
<td>7.1254</td>
<td>352.82</td>
</tr>
</tbody>
</table>

\[\ln (\gamma_m^a) = \frac{AAC}{T} + BAC - CAC \ln T\]

\[\ln (\gamma_w^0) = \frac{ABC}{T} + BBC - CBC \ln T\]

where,

- \(AAC = -11,732.8\)
- \(BAC = 240.65\)
- \(CAC = 34.344\)
- \(ABC = 3,638.3\)
- \(BBC = -61.59\)
- \(CBC = -9.115\)

\(T = \) liquid temperature in °K
Mass Transfer Coefficient

The value of the mass transfer coefficient for the dissolved component was obtained from the correlation by Sherwood and Holloway [1940]. Their work was based on experimental data obtained with 2-inch Raschig rings. The mass transfer coefficient obtained by the correlation can be considered typical for the same size packing in other forms such as Pall rings. The correlation is shown below:

\[
\frac{K_a}{\mathcal{D}} = \alpha \left( \frac{L'}{\mu} \right)^{1-\eta} \left( \frac{\mu}{\rho \mathcal{D}} \right)^{1-s} = \alpha (Re)^{1-\eta} (Sc)^{1-s}
\]

where for 2 inch Raschig rings

\[
\alpha = 1/0.012, \ \eta = 0.22, \ s = 0.5 \ \text{in range of}
\]

\[
L' = 400 - 15,000 \frac{\text{lbm}}{\text{ft.hr}}
\]

The infinite dilution diffusivity, \(\mathcal{D}\), of the dissolved component in water was obtained by the Scheibel prediction. This prediction was checked by agreement with Wilke-Chang and Othmer & Thaker prediction formulas.
Heat Transfer Coefficient

Solutions of many heat transfer problems can be obtained from corresponding problems of mass transfer at low mass-transfer rates. (Bird, 1960, pg. 642). Differential equations for heat and mass transfer can be written for situations of certain geometries and boundary conditions. Neglecting certain terms, the differential equations for the heat-transfer system and the mass-transfer system are analogous. This analogy allows the replacement of dimensionless mass transfer quantities with the analogous heat transfer quantities to convert a mass transfer correlation to a heat transfer correlation. Specifically, the Prandtl number $Pr = \frac{C_p \mu}{k}$ in heat transfer may be substituted for the Schmidt number $Sc = \frac{\mu}{\rho}$ in mass transfer. Likewise the Nusselt number for heat transfer without mass transfer $Nu = \frac{hD}{k}$ may be substituted for the Nusselt number for mass transfer for slow mass transfer. $Nu_{AB} = \frac{k_x D}{C_p AB}$.

Using these important analogies allows the prediction of the heat transfer coefficient for flow over 2 inch Raschig rings from the mass transfer correlation of Sherwood and Holloway.

$$\frac{k_x a}{\varphi} = \alpha(Re)^{1-\nu}(Sc)^{1-s} \quad \text{where} \quad k_x = k_L$$

Multiplying by $D/c$
To obtain the heat transfer correlation we substitute
\( \text{Nu} \) for \( \text{Nu}_{\text{AB}} \) and \( \text{Pr} \) for \( \text{Sc} \).

\[ \text{Nua} = \frac{D}{c} \alpha (\text{Re})^{1-\eta} (\text{Pr})^{1-s} = \frac{hD}{k} a \]

This gives

\[ \frac{h}{k} = \frac{\alpha}{c} (\text{Re})^{1-\eta} (\text{Pr})^{1-s} \]

Dividing the mass transfer correlation by this result we get

\[ \frac{k_{L}a}{\rho \text{pcp}} \frac{k}{ha} = c \frac{(\text{Sc})^{1-s}}{(\text{Pr})^{1-s}} \]

Since \( \alpha = \frac{k}{\rho \text{pcp}} \) in heat transfer is analogous to \( \beta \) we have

\[ ha = k_{L}a \frac{(\text{Sc})^{1-s}}{(\text{Pr})^{1-s}} \rho \text{pcp} \quad \text{or} \quad \frac{ha}{\rho \text{pcp}} (\text{Pr})^{1-s} = \frac{k_{L}a}{c} (\text{Sc})^{1-s} \]

This result has a similar form to the Chilton-Colburn analogy. The correlations differ in the value of \( s \).
Vapor Pressure

The vapor pressure data of a component was related to temperature by the following expression.

\[ \text{PST}(I) = \exp[\text{AVP}(I)/T + \text{BVP}(I)] \]

where

- \( \text{PST}(I) \) = vapor pressure of component I in mm Hg.
- \( T \) = liquid temperature in °K

Enthalpy

The enthalpy of liquid at 0°C was chosen as the reference state for which the enthalpy was taken to be zero. The liquid and vapor enthalpy for a given temperature differ by the heat of vaporization. The expressions relating the enthalpy of the liquid and vapor to temperature are given as follows.

\[ \text{HL} = \text{AHL}(I) + \text{BHL}(I) \times T \]
\[ \text{HV} = \text{AHV}(I) + \text{BHV}(I) \times T \]

where

- \( \text{AHL}(I) \) = constant to set reference state
- \( \text{BHL}(I) \) = mean heat capacity of liquid for component I
- \( \text{AHV}(I) \) = constant to set reference state plus the heat of vaporization for component I
- \( \text{BHV}(I) \) = mean heat capacity of vapor for component I
Justification of Assumptions Employed in the Mathematical Model of Steam Stripping

The assumptions employed in the mathematical modeling of the steam stripper can be summarized as follows.

1) The heat-transfer resistance was assumed to be entirely in the liquid phase. Thus the temperature of the vapor at any point in the column was assumed to be the value for the vapor at the interface.

2) The mass transfer was assumed to be controlled by liquid-phase diffusion. Thus the composition of the vapor at any point in the column was assumed to be the value for the vapor at the interface and the vapor phase was taken as saturated at interface conditions.

Assumption #1

Assuming that the heat-transfer resistance is entirely in the liquid phase is validated by the low heat capacity of the vapor. If temperature gradients did exist in the vapor phase (i.e., if the heat-transfer resistance is not entirely in the liquid phase), then there would still be no effect on the enthalpy balance due to the small heat capacity of the vapor stream. The temperature and steam flow in the column have been shown to be dominated by the enthalpy balance. Employing this assumption accounts for evaluation of interfacial concentrations, vapor pressures, and vapor enthalpies at interface temperature in equations 1, 2, and 4. The interface temperature was used as the vapor temperature in equations 5 and 6.
Assumption #2

The overall resistance to mass transfer consists of resistance in both the liquid and gas phase. In the modeling of the steam stripper it has been assumed that the gas-phase resistance is negligible. In the gas phase within the column, water is the major species. In the liquid phase the mole fraction of water exceeds 0.999. Because of these high mole fractions, any departure of the gas phase from equilibrium with the liquid surface would result in a high flux of water vapor. The effect is to greatly enhance the apparent diffusivity of the binary mixture. Because of this effect appreciable gradients cannot exist in the gas phase. If a small gradient develops the water moves to the interface very rapidly and condenses.

If the water cannot have a concentration gradient in our system because it is a condensable component at high concentration, then MIBK can have no concentration gradient because the system is a binary.
Appendix D

Experimental Data
Equilibrium data for the system Phenol-water-MIBK are presented in Tables D-1, D-2 and D-3. A plot of the distribution coefficient for phenol versus organic phase phenol concentration is contained in the text. The data point for the highest phenol concentration in the organic phase is thought to be inaccurate. It is believed that the equilibrium shifted between the time the aqueous and organic phases were analyzed. For purposes of fitting the equilibrium data to a smooth curve the following phase compositions were assumed to replace the inaccurate point at 50°C:

**Organic Phase** (denoted by *)

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>w</em>phenol</td>
<td>0.2000</td>
</tr>
<tr>
<td><em>w</em>H$_2$O</td>
<td>0.0335</td>
</tr>
<tr>
<td><em>w</em>MIBK</td>
<td>0.7665</td>
</tr>
</tbody>
</table>

**Aqueous Phase**

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>wphenol</td>
<td>0.0054</td>
</tr>
<tr>
<td>wH$_2$O</td>
<td>0.9841</td>
</tr>
<tr>
<td>wMIBK</td>
<td>0.0105</td>
</tr>
</tbody>
</table>
Table D-1

Experimental Equilibrium Data for Phenol-Water-MIBK at 30.0°C

<table>
<thead>
<tr>
<th>Organic Phase (denoted by *)</th>
<th>w Phenol</th>
<th>w H₂O</th>
<th>w MIBK</th>
</tr>
</thead>
<tbody>
<tr>
<td>w Phenol</td>
<td>0.0</td>
<td>.0513</td>
<td>.1006</td>
</tr>
<tr>
<td>w H₂O</td>
<td>.0204</td>
<td>.0242</td>
<td>.0291</td>
</tr>
<tr>
<td>w MIBK</td>
<td>.9796</td>
<td>.9245</td>
<td>.8703</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aqueous Phase</th>
<th>w Phenol</th>
<th>w H₂O</th>
<th>w MIBK</th>
</tr>
</thead>
<tbody>
<tr>
<td>w Phenol</td>
<td>0.0</td>
<td>.0004</td>
<td>.0012</td>
</tr>
<tr>
<td>w H₂O</td>
<td>.9818</td>
<td>.9846</td>
<td>.9850</td>
</tr>
<tr>
<td>w MIBK</td>
<td>.0182</td>
<td>.0150</td>
<td>.0138</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distribution Coefficients</th>
<th>K Phenol</th>
<th>K H₂O</th>
<th>K MIBK</th>
</tr>
</thead>
<tbody>
<tr>
<td>K Phenol</td>
<td>128.78±22.54</td>
<td>89.27±8.38</td>
<td>72.45±4.28</td>
</tr>
<tr>
<td>K H₂O</td>
<td>.0208</td>
<td>.0246</td>
<td>.0295</td>
</tr>
<tr>
<td>K MIBK</td>
<td>53.82</td>
<td>61.47</td>
<td>62.88</td>
</tr>
</tbody>
</table>

NOTE: Concentrations wᵢ, are in mass fraction.

Distribution coefficient = Kᵢ = (wᵢ*/wᵢ)± one standard deviation.
Table D-2

Experimental Equilibrium Data for Phenol-Water-MIBK at 50.0°C

<table>
<thead>
<tr>
<th>Organic Phase</th>
<th>(denoted by *)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w^*_\text{phenol}$</td>
<td>0.0</td>
</tr>
<tr>
<td>$w^*_\text{H}_2\text{O}$</td>
<td>.0244</td>
</tr>
<tr>
<td>$w^*_\text{MIBK}$</td>
<td>.9756</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aqueous Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w^*_\text{phenol}$</td>
</tr>
<tr>
<td>$w^*_\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$w^*_\text{MIBK}$</td>
</tr>
</tbody>
</table>

Distribution Coefficients

| $K_{\text{phenol}}$ | 72.59±11.43 | 53.49±2.77 | 44.21±1.97 | 41.36±1.85 |
| $K_{\text{H}_2\text{O}}$ | .0248 | .0273 | .0264 | .0316 | .0339 |
| $K_{\text{MIBK}}$ | 67.28 | 69.82 | 70.97 | 73.52 | 71.90 |

NOTE: Concentrations $w_i$ are in mass fraction.
Distribution coefficient $= K_i = (w^*_i/w_i) \pm$ one standard deviation.
Table D-3
Experimental Equilibrium Data for Phenol-Water-MIBK at 75.0°C

<table>
<thead>
<tr>
<th>Organic Phase (denoted by *)</th>
<th>0.0</th>
<th>.0438</th>
<th>.1014</th>
<th>.1492</th>
<th>.2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w_{\text{phenol}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( w_{\text{H}_2\text{O}} )</td>
<td>.0284</td>
<td>.0335</td>
<td>.0376</td>
<td>.0495</td>
<td>.0477</td>
</tr>
<tr>
<td>( w_{\text{MIBK}} )</td>
<td>.9716</td>
<td>.9227</td>
<td>.8610</td>
<td>.8013</td>
<td>.7506</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aqueous Phase</th>
<th>0.0</th>
<th>.0012</th>
<th>.0028</th>
<th>.0045</th>
<th>.0071</th>
</tr>
</thead>
<tbody>
<tr>
<td>( w_{\text{phenol}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( w_{\text{H}_2\text{O}} )</td>
<td>.9863</td>
<td>.9861</td>
<td>.9854</td>
<td>.9844</td>
<td>.9826</td>
</tr>
<tr>
<td>( w_{\text{MIBK}} )</td>
<td>.0137</td>
<td>.0128</td>
<td>.0118</td>
<td>.0111</td>
<td>.0103</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Distribution Coefficients</th>
<th>38.22±4.1</th>
<th>36.87±2.43</th>
<th>33.01±1.19</th>
<th>28.53±83</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_{\text{phenol}} )</td>
<td>.0288</td>
<td>.0340</td>
<td>.0382</td>
<td>.0503</td>
</tr>
<tr>
<td>( K_{\text{H}_2\text{O}} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{\text{MIBK}} )</td>
<td>70.92</td>
<td>72.08</td>
<td>72.77</td>
<td>71.93</td>
</tr>
</tbody>
</table>

NOTE: Concentrations \( w_i \) are in mass fraction.

Distribution coefficient = \( K_i = (w_i^*/w_i) \pm \) one standard deviation.
Appendix E

Basis for Cost Estimates
The estimates of capital and operating costs for the three processes considered were made on a consistent basis. The capital cost estimates make use of the prediction technique of Guthrie (Chemical Engineering, March 24, 1969) and the operating cost estimates employ the methods presented by Peters & Timmerhaus. (Plant Design and Economics for Chemical Engineers, 2nd. ed., McGraw Hill Book Company, 1968.) To include the effect of inflation, all costs were expressed in 4th-quarter 1978 dollars by using the M & S chemical process industry cost index.

Capital Cost

The "module" technique of Guthrie was used to estimate the installed cost of each plant. Material and energy balances were based on the assumptions listed on page in the text. The major pieces of off-site equipment were then sized and their cost determined from the cost diagrams of Guthrie. For items of equipment that could not be costed from the diagrams of Guthrie, the cost from other sources was used in a manner as consistent with Guthrie as possible.

Guthrie gives, for each type of equipment, factors which are multiplied by the purchase price of the item to yield an estimate for the auxiliary equipment (piping, concrete, instruments, etc.) cost, the labor cost for material erection and equipment installation, and the indirect (freight, construction overhead, engineering, etc.) costs. The total factors for each type of equipment
are typically 3.29 to 4.23 for process equipment. The allocated capital for off-site facilities was determined from the following charges:

- Steam, 220 psig, saturated: $1.94/1000lb/yr
- Electricity: 3.5¢/kW-hr/yr
- Recycled cooling tower water: $0.43/1000gal/yr
- Tankage for 7 days of recovered phenol: $73,750 (1978)

This installed equipment total cost was increased by 18% for contingency and contractor's fee. No costs were included for site development or industrial buildings. The off-site facilities cost includes allocated capital for steam, recycled cooling tower water and electricity. Storage tanks for the recovered phenol were also included. The working capital consists only of the solvent inventory. The recovered pollutant inventory is considered to have negligible impact on the need for working capital.

The total of the costs above is referred to as the Total Plant Investment in the text. The percentage of this total is listed for each major on-site or off-site item of equipment.

**Annual Operating Cost**

The plant is assumed to operate with an on-stream factor of 90 percent. The following items are included in the operating costs (Peters and Timmerhaus, 1968):
1. Utilities - The outlet water can be used as make up for a cooling water system to supply all the plant's requirements. Therefore, the cooling water cost is for recycled cooling-tower water. The following values were used for the costs of steam, electricity and recycled cooling water:

- Steam @ 200 psig, saturated: $3.30/1000 lb
- Electricity: 2.4¢/kWhr
- Recycled Cooling Tower Water: 14.¢/1000 gal.

2. Raw Materials - The cost of solvent to make up for losses in the treated water, recovered pollutant and vacuum system was included at the market price of the solvent.

3. Labor - Operating labor costs were taken as $7.00 per manhour.

4. Labor Dependent Items -

<table>
<thead>
<tr>
<th>Annual Cost</th>
<th>Percentage of Operating Labor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supervisory and Clerical Labor</td>
<td>15</td>
</tr>
<tr>
<td>Administration</td>
<td>15</td>
</tr>
<tr>
<td>Plant Overhead</td>
<td>70</td>
</tr>
<tr>
<td>Laboratory</td>
<td>15</td>
</tr>
</tbody>
</table>
5. Total Plant Investment (TPI) Dependent Costs -

<table>
<thead>
<tr>
<th>Annual Cost</th>
<th>Percent of TPI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maintenance and Repairs</td>
<td>6</td>
</tr>
<tr>
<td>Operating Supplies</td>
<td>1</td>
</tr>
<tr>
<td>Depreciation</td>
<td>10</td>
</tr>
<tr>
<td>Insurance and Taxes</td>
<td>3</td>
</tr>
<tr>
<td>Finance Cost (value of money)</td>
<td>15</td>
</tr>
</tbody>
</table>

No general expenses (distribution and selling costs, research and development) were included in the estimate of operating cost except for administrative cost, which was included as a labor dependent cost. The previously stated costs can be summarized in a single equation as follows:

\[
\text{Annual Gross Operating Cost} = \text{Raw Materials} + \text{Utilities} + 2.40 \times (\text{Labor Costs}) + 0.35 \times (\text{TPI})
\]

The annual net operating cost is equal to the annual gross operating cost minus the phenol by-product credit. This credit is figured at 15 cents per gallon of the phenol mixture.

In the text, the total operating cost is listed as a value per thousand gallons of waste water treated. This credit is calculated by dividing the annual operating cost by the number of gallons of quench water treated per year. The individual costs of the annual operating costs are also listed as a percentage.
Figure 1 - Schematic diagram of solvent extraction of waste water.
Figure 2 - Flow Diagram of the Distillation Process

1. Filter
2. Countercurrent Multi-Stage Solvent Extractor
3. Phenol Containing Ether Pump Tank
4. Crude Phenol Oil-Liquor-Decantation Tank
5. Ether Pump Tank
6. Dephenolized Liquor Tank
7. Crude Phenol Pump Tank

---

Phenolized Ammonia Liquor
---

Isopropyl Ether
---

Coke Oven Gas
---

Crude Phenol Oil
---

Steam
---

Ammonia Still Waste (90°C)
---

Cooling Water
Figure 3 -
Phenol - water - MIBK system

\[ K_m = \frac{W'_{\text{phenol (in organic phase)}}}{W_{\text{phenol (in aqueous phase)}}} \]

Figure 4 -
Column press: 9.55 kN/m²
Feed conc: 15000 ppm
Effluent conc: 2 ppm
Column height: 6 m

To Total overhead vapor flow (moles/mole of liquid feed)

Feed temperature (°C)

Figure 8 -
\[ J = 1 \]
\[ J = 2 \]
\[ J = 3 \]
\[ J = 4 \]
\[ J = N J - 2 \]
\[ J = N J - 1 \]
\[ J = N J \]

\[ z = 0 \]
\[ z_0 \]
\[ \Delta z \]

\text{Figure A-1 - XBL794-1136}
Number of unknowns at each $J = (n+1)x, (n+1)y, T_L, T_V, L, V, P$

$J = 1$
- $n$ Specification of $x$ for dissolved components
- 1 Specification of $T_L$
- 1 Specification of $L$
- 1 Specification of $P$
- $n$ Mass balances for dissolved components from $J$ to $J+1$ (Equation 3)
- 1 Heat transfer relation from $J$ to $J+1$ (Equation 5)
- 1 Vapor saturated with $H_2O$ at $T_V$ (Equation 2)
- 1 $\sum x = 1$ (Equation 7)
- 1 $\sum y = 1$ (Equation 8)

$1 < J < NJ$
- $n$ Mass transfer relations for dissolved components from $J-1$ to $J$ (Equation 1)
- $n$ Mass balances for dissolved components from $J$ to $J+1$ (Equation 3)
- 1 Mass balance for $H_2O$ from $J-1$ to $J$ (Equation 3)
- 1 Heat balance from $J-1$ to $J$ (Equation 4)
- 1 Heat transfer relation from $J$ to $J+1$ (Equation 5)
- 1 Vapor saturated with $H_2O$ at $T_V$ (Equation 2)
- 1 Pressure drop from $J-1$ to $J$ (Equation 6)
- 1 $\sum x = 1$ (Equation 7)
- 1 $\sum y = 1$ (Equation 8)

$J = NJ$
- $n$ Mass transfer relations for dissolved components from $J-1$ to $J$ (Equation 1)
- 1 Mass balance for $H_2O$ from $J-1$ to $J$ (Equation 3)
- 1 Heat balance from $J-1$ to $J$ (Equation 4)
- 1 Specification of $V$
- 1 Pressure drop from $J-1$ to $J$ (Equation 6)

If $V \neq 0$
- $n$ Specifications of $y$ for dissolved components ($= 0$)
- 1 Specification of $T_V$
- 1 $\sum x = 1$ (Equation 7)
- 1 $\sum y = 1$ (Equation 8)

Figure A-2 - Ordering of Relationships Modeling the Packed Column
Feed temperature: 30°C
Feed conc: 6300 ppm BuAc
Column height: 4 m

Figure A-3 - XBL 794-1130
Stage 1
L(1) \downarrow \quad V(1)

Stage 2
L(2) \downarrow \quad V(2)

Stage N-1
L(N) \downarrow \quad V(N)

Stage N
L(N+1) \downarrow \quad V(N+1)

Figure B-1
Figure B-2 -
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