

SOLVENT RECOVERY BY BATCH FRACTIONATION FROM TOXIC LABORATORY LIQUID WASTES*

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ABSTRACT

Batch fractionation is employed in the present study to recover chemical solvents from highly toxic and concentrated liquid wastes generated in a chemical analytical laboratory. The chemical solvents recovered are of sufficient purity for reuse. Properly designed batch fractionation apparatus is economically attractive for dealing with these kinds of toxic liquid wastes.

INTRODUCTION

Liquid waste from a chemical analytical laboratory is one of the most common industrial wastewaters. Very often this liquid waste contains considerable amounts of strong acids and bases, and toxic organic and inorganic compounds [1, 2]. Disposal of this liquid waste represents a difficult task because it can not be treated by conventional biological treatment [3, 4] or by simple physical or chemical methods [1, 2]. The reasons are that the liquid waste is very often highly toxic not only to the microorganisms in the activated sludge, but to human beings as well. Furthermore, many refractory organics may also exist in this waste, rendering it doubly difficult for activated sludge processes or physical and chemical processes.

Currently, the common industrial practice to deal with this liquid waste is by incineration [1]. This technique will be acceptable if the incineration temperature

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is sufficiently high enough to render the hazardous chemical constituents nontoxic [1, 2]. Such a high temperature incinerator however is expensive to operate and maintain and often is not readily available to most potential users. Lower temperature incineration of this liquid chemical waste can cause serious air pollution problems, especially when the liquid waste contains toxic chlorinated organic compounds. This problem of toxic liquid waste disposal exists in Taiwan as well as in many countries around the world. Therefore, an economic and effective alternative is urgently needed.

From the economic standpoint, waste disposal of any kind is an expensive practice. The most economic approach to this disposal problem is reduction of waste production at source, which minimizes waste disposal costs outright. Resource recovery, in which valuable materials are recovered from a waste disposal process, can also be worthwhile economically. The materials recovered may be reused, helping to defray part of the waste disposal costs. This article assesses a resource recovery technique for certain chemical laboratory liquid wastes, using batch fractionation for solvent recovery. The recovered solvents are sufficiently pure for reuse. The apparatus for batch fractionation is relatively simple and inexpensive, and the process can easily be adopted by industrial and other users who encounter similar problems. The fractionation method appears to be significantly more economical than incineration for dealing with laboratory liquid waste.

LIQUID WASTE SOURCES AND COMPOSITION

The liquid chemical waste is generated in the analytical laboratory of a large chemical fiber plant. The main product of the plant is polyester fiber, that is synthesized by polycondensation of ethylene glycol and terephthalate under partial vacuum conditions. The quality of polyester fiber must be strictly controlled in order to assure proper ensuing processing of those fibers. The quality of polyester is measured in terms of its viscosity and the degree to which the functional $-\text{COOH}$ group remains in the fiber. The three kinds of wastes herein reported are the acid value liquid waste (AV), the relative viscosity liquid waste (LV) and the intrinsic viscosity liquid waste (IV). Table 1 shows their major constituents. All chemical solvents used to prepare the liquids are more than 99.99 percent pure. Approximately 14 liters of each of the three liquid wastes are produced daily in the analytical laboratory. The wastes are highly toxic and have strong, pungent odors. Currently, they are incinerated with other solid wastes generated in the plant at about 1000° which is deemed insufficient to decompose all toxic chemical constituents [1, 2]. The air pollution caused by the incineration poses a major regulatory problem to the manufacturer. Several chemical and physical treatment alternatives have been explored and carefully evaluated in regards to their economic and technical merits. The batch fractionation method represents the final selection and appears to be the most attractive option.

Table 1. Chemical Compositions of Three Liquid Wastes

1. Acid Value Liquid Waste
Original liquid consisting of pure phenol and trichloromethane mixed together in 2:3 weight ratio.
2. RV Liquid Waste
Final liquid waste consisting of 5 g of polyester dissolved in 500 ml m-cresol plus some indicator.
3. IV Liquid Waste
Original liquid consisting of pure phenol and tetrachloroethane mixed together in 2:3 weight ratio
Final liquid waste containing 3 g of polyester dissolved in 500 ml of the original liquid

SOLVENT RECOVERY

Incineration and other chemical treatments destroy the chemical components of the liquid wastes [1]. In batch fractionation method, chemical solvents are recovered in such high purity that these very expensive solvents can be reused.

Batch fractionation is a type of distillation [5, 6]. This method is rarely considered or used as an unit operation among physical treatment methods for toxic liquid wastes. A typical batch fractionation column is shown in Figure 1. The boiler at the bottom is charged with the waste liquid mixture to be distilled. The waste liquid is partially converted to vapor by a heater. The vapor formed in the boiler is richer in components with lower boiling point (also called the "light" components) than the unvaporized liquid. To increase the concentrations of light components in the vapor, the vapor stream is brought into intimate countercurrent contact with a descending liquid stream, called the reflux, in the reflux column. The reflux entering the top of the column is immediately heated to its boiling point by the vapor, and throughout the column liquid and vapor are at their boiling and condensing temperatures, respectively. As the vapor stream ascends in the column, its light component content increase. The basic principle of fractionation exploits differences in volatility of the components in the liquid mixture. By varying the heating temperatures in the boiler, all volatile chemical solvents can in principle be driven off the waste liquid mixture one at a time and thus recovered as pure components. As shown in Table 2, there is a significant difference in the boiling points (at one atmospheric pressure) of the major chemical components in the liquid wastes. Hence batch fractionation is a potential method for liquid wastes with prevailing volatile compounds.

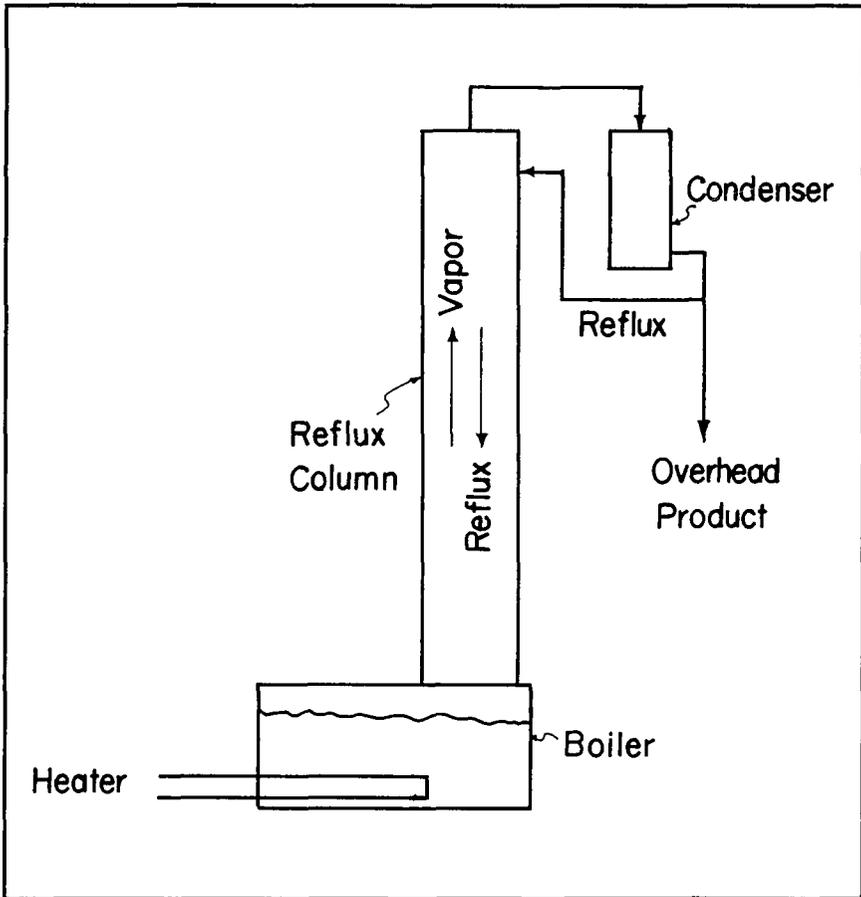


Figure 1. Standard batch fractionation column.

Table 2. Normal Boiling Points of Various Organic Solvents [7]

Trichloromethane	61.5°C
Tetrachloroethane	146.5°C
Phenol	182.0°C
m-Cresol	202.0°C

FRACTIONATION OF THE LIQUID WASTES

The apparatus used for the present batch fractionation study is shown in Figure 2. An electric heater with a Variac control was used to control the fractionation temperature. The plexiglass fractionation bottle had a maximum capacity of 1 liter. A reflux tube of 9 cm was attached to the fractionation bottle. A thermometer was inserted at the top of the reflux tube to monitor the vapor temperature. A condenser tube was then connected to the reflux tube for condensing the boiled-off vapor. Tap water or warm water was employed in the condenser. The condensate was collected in a collection bottle for analysis.

Since the RV liquid waste contains only one volatile component, it was not too difficult to separate this component from the mixture. About 365.5 g of the RV liquid was placed in the fractionation bottle at room temperature and the electric heater set at 202° (the normal boiling point of m-cresol). At 95°C, the liquid in the bottle started to boil. The first drop of liquid from the condenser appear at 135°; during the fractionation period, the vapor temperature remained constant at 202°C. Collection of the condensate continued until no more liquid was condensed. The collected liquid was clear and weighed 331 g (or 90.6% recovery

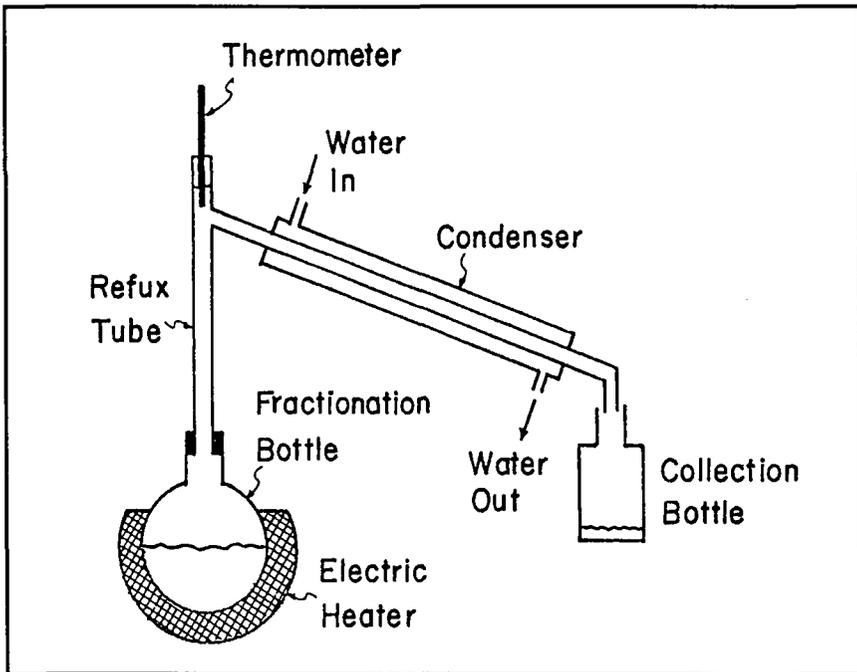


Figure 2. Batch fractionation apparatus for toxic liquid wastes.

based on the total initial mass). Using a Hewlett Packard gas chromatograph (GC) for sample analysis, the liquid was found to be 100 percent pure *m*-cresol. The remaining residue was a highly viscous, dark brown fluid containing melted polyester and a small amount of *m*-cresol. The residue was disposed of by solidification with flyash cements; this aspect will be discussed in detail in a separate report.

The acid value liquid waste consists of two major volatile components: phenol and trichloromethane (also known as chloroform), and small amounts of other components. Batch fractionation of this liquid was conducted as before by initially charging 355 g to the fractionation bottle and setting the heater at 182°C (the higher boiling point of the two major components). Boiling started around 55° and during the boiling period, the temperature remained at 61°C. As the boiling stopped, about 189 g of clear liquid were collected. The collected liquid was analyzed by GC to be pure trichloromethane.

After the first stage boiling was completed, the liquid temperature started to rise. At 110°C, it began to boil again. This time about 21 g of a second clear liquid was collected. Analysis of this liquid revealed that it contained 10.3 percent trichloromethane, 89.5 percent phenol and 0.2 percent impurities. During this period, the temperature remained essentially constant. After the second boiling, the liquid temperature began to climb to 180°C. At that temperature, white crystals appeared on the condenser tube wall. It was suspected that the crystal was pure phenol. According to the Merck Index [7], pure phenol crystallizes at 40.83°C. Tap water around the condenser tube kept the condenser temperature below 40°C and hence caused the pure phenol to crystallize. To melt the solid crystal, warm water around 55°C was fed to the condenser instead. The temperature was sufficient to condense the phenol vapor and yet keep it from crystallizing. The liquid collected in the collection bottle however crystallized very rapidly; analysis of the melted crystal sample by the Shimadzu gas chromatograph confirmed that it was pure phenol. Overall, 115.2 g of pure phenol were gathered in this stage. Finally, the highly viscous residue, which contains a large proportion of melted polyester, weighed about 29.6 g. It was black and still possessed a faint pungent smell, presumably because of the remaining small amounts of trichloromethane and phenol.

The two major volatile components in the IV liquid waste were phenol and tetrachloroethane. Table 2 shows that the normal boiling points of these two components are significantly closer to each other than those of the acid value liquid waste. The closer the normal boiling points, the more difficult it is to separate them into pure components. This was the case with the IV waste liquid.

Three hundred fifty-four g of the IV liquid waste was placed in the fractionation bottle with the electric heater set at 182°C. At 140°C, a clear liquid of 221.1 g was gathered at that constant temperature using cold tap water for condensation. Then,

at 180°C, another 108.7 g of crystals was collected in the collection bottle with warm condensing water. The crystal was also found to be pure phenol. The clear liquid collected at 140°C was determined to contain 53.9 percent tetrachloroethane, 44.8 percent phenol and 1.3 percent impurities, confirming the earlier suspicion that the closer normal boiling temperatures might cause some fractionation problem. The black, pungent residue weighed 24.1 g and was highly viscous.

EFFECT OF THE LENGTH OF REFLUX TUBE

In the batch fractionation experiments, the m-cresol and the majority of trichloromethane and phenol were recovered in high purity form the liquid wastes. However, distilled liquid mixtures were still obtained for the acid value and the IV liquid wastes. Those mixtures need to be refined or fractionated in order to obtain pure components. A better alternative is to fractionate the original liquid wastes with a longer reflux tube. In the original fractionation apparatus, the reflux tube was 9-cm long. A longer reflux tube would be beneficial to the batch fractionation since it would provide a much longer residence time. This would let the "heavier" component(s) with higher normal boiling point to condense back to the fractionation bottle and let the "light" component go to the condenser [5, 6]. An extension of this argument is that if the reflux tube is sufficiently long, all mixtures can theoretically be separated into pure components as long as there are differences in normal boiling points among all volatile components. To investigate this point, the length of the reflux tube was doubled to 25 cm and the acid value IV waste liquids were batch fractionated again.

With the extended reflux tube, the volatile components in the acid value liquid waste were separated into pure components in two stages. The first stage (at 80°C) yielded pure trichloromethane and the second stage (at 180°C) produced pure phenol. The liquid mixture generated between these two temperatures in the batch fractionation with short reflux tube did not occur in this case.

A batch fractionation with extended reflux tube was performed for the IV liquid waste. The second stage of fractionation produced pure phenol. The liquid collected in the first stage was still a mixture. However, the tetrachloroethane concentration in the mixture was improved considerably, from 53.9 percent to 95.4 percent, suggesting that the 25-cm reflux tube still is not long enough for this particular liquid waste. Further extension of the reflux tube was needed. The reflux tube was then extended to 35 and 45 cm. The corresponding tetrachloroethane concentrations were found to be 99.4 and 100 percent, respectively, successfully eliminating phenol from the tetrachloroethane at 140°C. The impurity in tetrachloroethane as a function of the length of the reflux tube is shown in Figure 3.

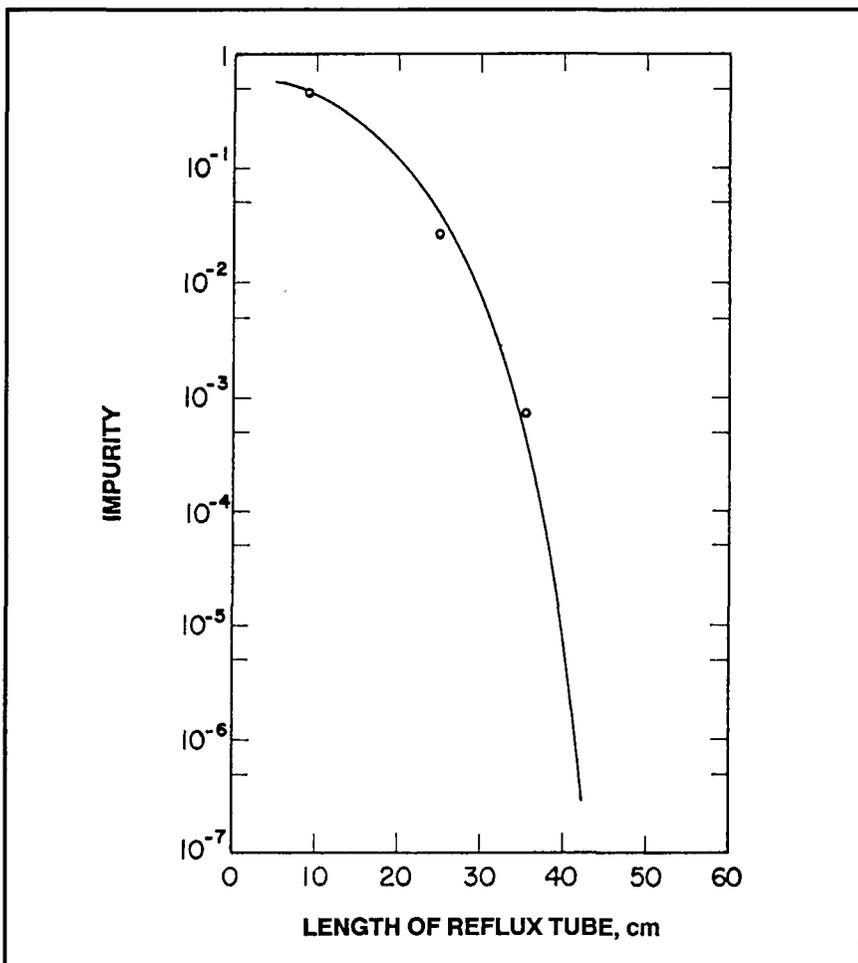


Figure 3. Change of impurity in tetrachloroethane percentage as a function of the length of the reflux tube.

CONCLUSIONS

A simple batch fractionation apparatus effectively separated chemical solvents from toxic laboratory liquid wastes into pure volatile components. By appropriate selection of the length of reflux tube, it has been shown that it is possible to recover pure chemical solvents for reuse. The method is relatively easy to carry out. For small amounts of liquid wastes, batch fractionation is satisfactory. However, if large quantities of liquid waste are generated, it would be more

appropriate to consider a continuous fractionation process. Modification of the present apparatus for continuous operation would not be difficult.

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