

## Recovery of Acetic Acid From Effluent via Freeze Crystallization

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### Abstract

*Freeze crystallization is an efficient separation process that can potentially be used in any application. Freeze crystallization is a high energy efficiency separation process that can be applied to a wide variety of industrial requirements. Although the vapor-liquid equilibrium is generally employed to separate the components of a solution, use of solid-liquid equilibrium should be considered – it may be cheaper. This paper describes a case study of recovery of acetic acid from effluent via freeze crystallization. Complete recovery of acetic acid from acetic acid-water solution by ordinary distillation is nearly impossible, because relative volatility of this mixture in the range of 1-30% of acetic acid in water is very close to one. But the same separation is possible by freeze separation technique and it is found experimentally that large amount of acetic acid (about 71.5%) can be recovered via freeze separation technique. Also it is found that the energy required for recovery of acetic acid is much lower (about 24 times) than that of distillation.*

Key words – Eutecic freeze crystallization, Solid-liquid equilibrium, Recovery of acetic acid, Heat of sublimation

### 1. Introduction

The two major problems currently facing are firstly: the declining availability of sufficient quantities of water, and secondly: the deterioration of the quality of the available water. However, with the increasing use of water recycling technology such as desalination, ion exchange regeneration, inorganic precipitation, biological processes and membrane treatments, the result has been an increased generation of inorganic brines and concentrates.

Handling aqueous salt-bearing streams, either for the recovery of the salt, or for the reduction of waste streams via a concentration process, is energy intensive and thus costly. Because the heat of fusion of ice (6.01 kJ/mol) is six times less than the heat of evaporation of water (40.65 kJ/mol), the energy required to separate the water as ice is significantly less than that required to separate it by evaporation, although obviously the energy for freezing will be more expensive than that for heating. Freeze crystallization has been used historically in those applications where other separation processes are incapable of effecting the separation. Although freeze crystallization has

been used to fractionate solution in specialized applications, the technique has never been adopted on a large scale. In some applications, freezing can perform a separation with 75-90% reduction of the energy required by convention distillation – acetic acid and acrylic acid refining are two examples.

Freeze crystallization also shows significant energy reduction in many applications for which evaporators are commonly employed. Energy consumption of paper-plant black-liquor evaporators could be reduced by a half by using freezing. Freeze separation is not the answer to every separation problem. Under some circumstances, either capital cost or energy consumption can be excessive.

The current paper presents case study of acetic acid recovery from effluent via freeze separation technique. The separation is done in four stages. The paper also presents the loss and recovery of acetic acid experimentally and stage wise energy (heat of sublimation) required for the same.

### 2. Eutectic Freeze Crystallization (EFC)

In a binary mixture, a point is eventually reached where both components crystallize simultaneously: this is called the eutectic point and the crystallization carried out at eutectic point is called Eutectic Freeze Crystallization (EFC).

Eutectic Freeze Crystallization is an extension of freeze crystallization where the solution is cooled to the specific EFC conditions. Ice and salt continue to form at the eutectic temperature and below until no solid liquid phase is left. Eutectic Freeze Crystallization can be applied to solutions of any concentration but it is best to operate with concentrations near the eutectic point. Eutectic Freeze Crystallization is a more recently developed technology, where water and salts are separated by reducing the temperature to the eutectic temperature. The big advantage of EFC compared with other separation processes between water and salt is that EFC is more energy efficient, even up to 90%.

Eutectic freeze crystallization (EFC) is an alternative technology for the separation of highly concentrated aqueous streams. Eutectic Freeze Crystallization is a technique that is capable of separating aqueous solutions into pure water and pure-solidified solutes and that is highly energy efficient, without the introduction of any solvents. In addition, the simultaneous production of pure ice and pure salt(s) is a major advantage.

The principle of the process is as: when a solution containing dissolved contaminants is slowly frozen, water ice crystals form on the surface, and the contaminants are concentrated in the

remaining solution (the mother liquor). The ice crystals can be separated from the mother liquor, washed and melted to yield a nearly pure water stream. The mother liquor will contain a pure salt, which crystallizes at the eutectic temperature. Theoretically, a 100% yield can be obtained in a binary system, which is one of the advantages of EFC technology. Pure water and salt can be simultaneously recovered from aqueous solutions by EFC at low energy costs and very high yields. This, however, has never led to an industrial application for EFC because the process is currently uneconomical.

The energy reductions under EFC operation are found to be 30% - 65% when compared to conventional multi-step evaporation. EFC can also in principle achieve a 100 percent separation of the solution into ice and salt, provided no purge stream is needed. Corrosion of construction materials is also subsequently reduced because of the low operating temperatures. The technology can also treat a wide variety of feed solutions without the addition or need of adding further solvents or chemicals.

EFC technology has low energy requirements and theoretically the feed can be completely converted to water and solidified solutes. The most prominent disadvantages of EFC are investment costs and scale limitations but the current view is that these can be overcome. The current goal is to develop eutectic freezing equipment for industrial scale. The ice and salt crystals need to have a high purity, should be easily separable and should be economically viable to compete with conventional separation techniques.

### 3. Solid-Liquid Equilibrium

All freeze separation processes are based on the difference in component concentrations between solid and liquid phases that are in equilibrium. This can be most easily understood by referring to Figure 1. As the solution (say, at point A) is cooled, there will be some temperature at which a solid crystalline phase begins to appear in liquid phase (Point B).

Usually only one component in the solution is crystallizes, and that crystal is pure. This permits operation in a single theoretical stage. The energy efficiency of the freeze separation process results both from this single-stage capability and from the lower latent heats associated with the solid-liquid phase change; crystallization latent heats are one-half to one-tenth those of vaporization.

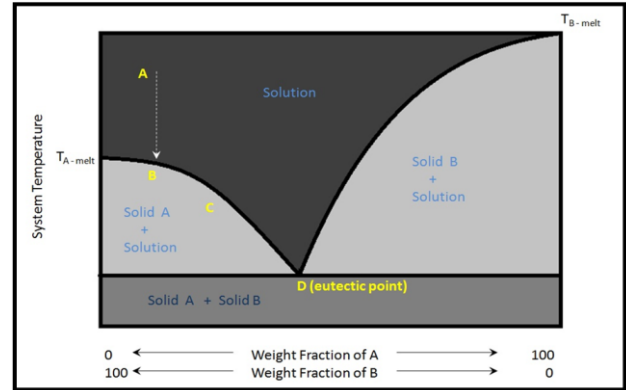


Figure 1. Simple Binary Solid-Liquid Equilibrium Diagram

At the initial freezing temperature, only a small amount of crystal will be formed. As crystals of a component are formed, the concentration of that component remaining in the solution is decreased. This causes the crystallization temperature of the remaining liquid to drop minutely, so that a lower operating temperature is needed to further crystallization. Thus, higher conversions to crystal phase require successively lower temperatures, as shown by the operating line BCD.

In a binary mixture, a point is eventually reached where both components crystallize simultaneously: this is called the eutectic and is shown as point D. At the eutectic, the concentrations of solid and liquid phase remain constant.

#### 3.1 Acetic acid-water binary solid liquid equilibrium

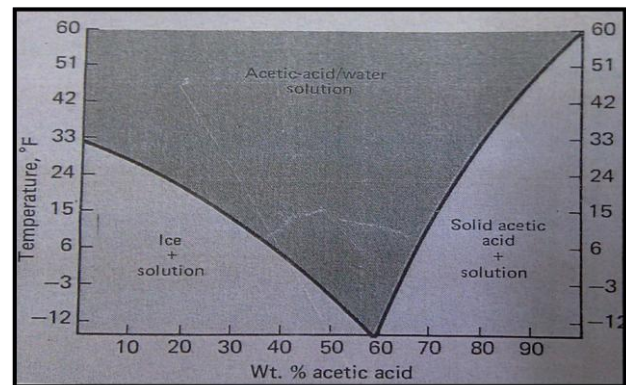
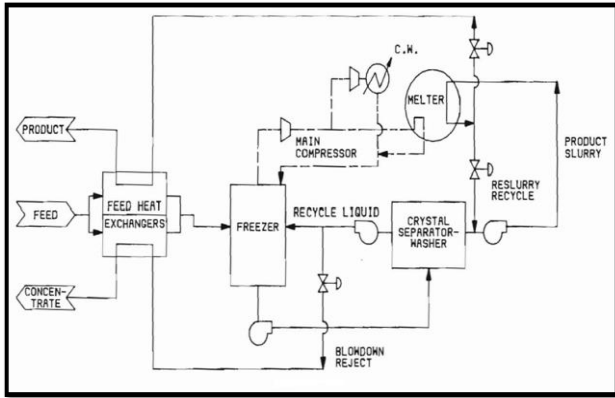


Figure 2. Acetic acid-Water SLE Diagram

The Acetic acid-water binary system and the data available in the literature are summarized in Figure 2. It is noted that the eutectic point of acetic acid-water system is at 59% acetic acid and -16 °F (-26.67 °C).

### 4. Freeze Separation Technology

A general process schematic of the freeze crystallization separation process is shown in Figure 3.



**Figure 3. Freeze Crystallization Process Diagram**

#### 4.1 Components of freeze process system

- Freezer (or crystallizer): A freezer, where a portion of the liquid is changed to the solid phase by removing heat. Or where, sufficient heat is removed from the process fluid to crystallize up to 15% of the mass.
- Separator (Crystal purifier): A crystal purifier, where the crystal phase is separated from the remaining liquid, and the crystals are washed to remove adhering concentrate from the surface. The separated concentrate is recycled to the freezer to provide any desired recovery. The Separator can be a centrifugal device, a filter, a screen, or a vessel called a wash column.
- Refrigeration Cycle (Heat pump): A heat pump that takes heat out of the freezer and transfers it either to cooling water or to the melting crystal that is removed from the purification section.
- Feed heat Exchanger: A feed heat-exchanger is employed to recover the 'cold energy' from the process streams, for cooling the fresh feed material. In other word, it is used to pre-cool the feed by using the cold product and concentrate, thus reducing the load on the freezer.

#### 4.2 General operating mode

- Feed enters the process through heat exchangers where the cold is recovered from the product and concentrate streams exiting the system. This feed then enters the freezer or crystallizer where a portion of it is converted to a solid, relatively small (100 to 500 microns) crystals.
- The crystals are pumped as slurry from the freezer to a separator which removes the liquid from the slurry, and usually washes the crystals with a small portion of

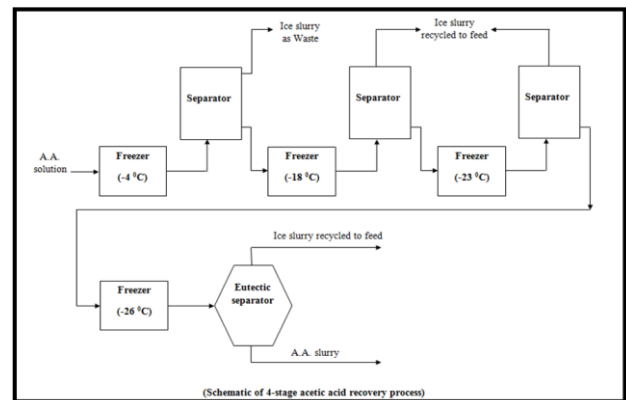
either melted product or some suitable wash material that will not dissolve the crystal.

- Most of the liquid is recycled to the freezer where more of the desired constituent is recovered. The washed crystal is then melted, either directly in contact with the refrigerant or through a heat exchange surface.
- Part of the melted product can be recycled to re-slurry the washed crystal, as necessary. The net product flow is pumped through the feed exchanger and out of the system.
- The refrigeration equipment removes heat from the freezer and transfers it to the melter, with any excess heat being removed from the system through the heat rejection compressor.
- The Freezer removes sensible heat to cool the feed down to the freezing point, and then latent heat to convert liquid to solid.

## 5. Experimental Studies

### 5.1 Experimental Procedure

The eutectic point of acetic acid from the data is  $-26^{\circ}\text{C}$ . So to reach the point the system is divided in four stages (Stage 1:  $-4^{\circ}\text{C}$ , Stage 2:  $-18^{\circ}\text{C}$ , Stage 3:  $-23^{\circ}\text{C}$ , Stage 4:  $-26^{\circ}\text{C}$ ) as shown in fig 3.



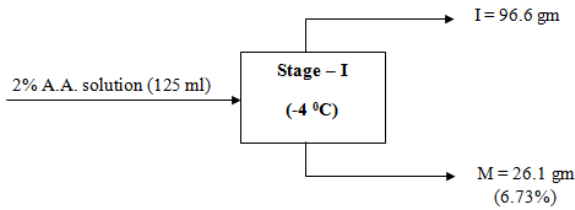
**Figure 4. Acetic acid recovery process diagram**

Initially taken feed solution of 2% acetic acid and is frozen up to  $-4^{\circ}\text{C}$ . Ice is separated out and the filtrate is taken to the second stage in which it is frozen to  $-18^{\circ}\text{C}$ . The same procedure is repeated for third stage ( $-23^{\circ}\text{C}$ ) and fourth stage ( $-26^{\circ}\text{C}$ ). The acetic acid is lost only from the first stage as ice slurry. The ice slurry from other stages except first stage is proposed to recycle to the feed solution. After each stage ice is separated out and the filtrate is analyzed.

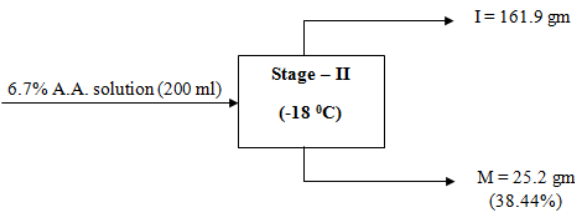
### 5.2. Results

#### 5.2.1 Stage wise Results

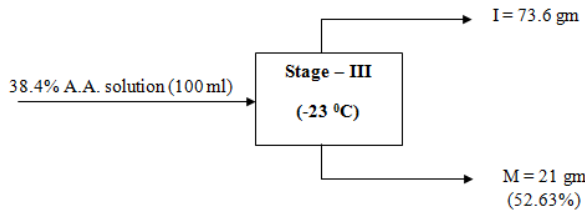
Stage I



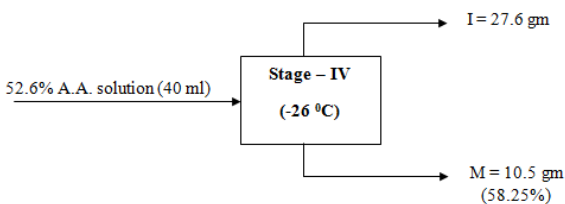
Stage II



Stage III



Stage IV



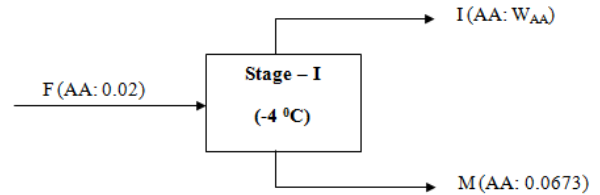
5.2.2 Trial wise Results

**Table 1. Concentration of Acetic Acid after each trial and each stage**

Stage	Temp. (°C)	Concentration of Acetic acid (%)			
		1 <sup>st</sup> trial	2 <sup>nd</sup> trial	3 <sup>rd</sup> trial	Average
I	- 4	6.82	6.51	6.86	6.73%
II	- 18	37.94	38.81	38.57	38.44%
III	- 23	52.40	51.90	53.59	52.63%
IV	- 26	58.50	57.85	58.40	58.25%

5.2.3 Loss of Acetic acid

The acetic acid is lost only from first stage as the ice slurry from second, third and fourth stages are proposed to recycle to the feed solution.



Basis: 1 kg feed

Overall M.B. :  $F = I + M$

AA Balance :  $(0.02)(1) = (I)(W_{AA}) + (M)(0.0673)$

Also, from the result of stage I:  $I/M = 3.7$

$M = 0.2127, \quad I = 0.7843, \quad W_{AA} = 0.00725$

% Loss of AA = 28.43%

% Recovery of AA = 71.57%

5.2.4 Stage wise heat of sublimation required

Basis: 1000 kg of 2% Acetic acid

Heat of fusion of ice = 6.01 KJ/mol

**Table 2. Heat of sublimation for each stage**

Stage	Heat of Sublimation required (KJ)
I	258.03
II	56.44
III	6.46
IV	1.272
Total	322.20 KJ $\approx$ 350 KJ

For the same separation, energy required by reboiler of distillation column is approximately 8700 KJ<sup>(6)</sup>.

**6. Conclusion**

Wastes have been considered to be a serious worldwide environmental problem in recent years. Because of increasing pollution, these wastes should be treated. However, industrial wastes can contain a number of valuable organic components. Recovery of these components is important economically. Using conventional distillation techniques, the separation of acetic acid and water is both impractical and uneconomical, because it often requires large number of trays and a high reflux ratio.

In practice special techniques are used depending on the concentration of acetic acid. Complete recovery of acetic acid

from acetic acid-water solution by ordinary distillation is nearly impossible, because relative volatility of this mixture in the range of 1-30% of acetic acid in water is very close to one. For this range, either liquid-liquid extraction or azeotropic distillation is conventionally used. But same require high cost. Same can be possible economically by using freeze separation technique. So, for very dilute stream of acetic acid in water (effluent stream), freeze crystallization seems to be more economical technique. Also it is found experimentally that about 71.5% of acetic acid can be recovered by using freeze separation technique. It is also found that for recovery of acetic acid (1000 kg of 2% acetic acid), the energy (heat of sublimation) required by freeze separation (350 KJ) is much lower (about 24 times) than that of distillation (8700 KJ). Hence the recovery of such organic acid becomes important environmentally as well as economically.

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