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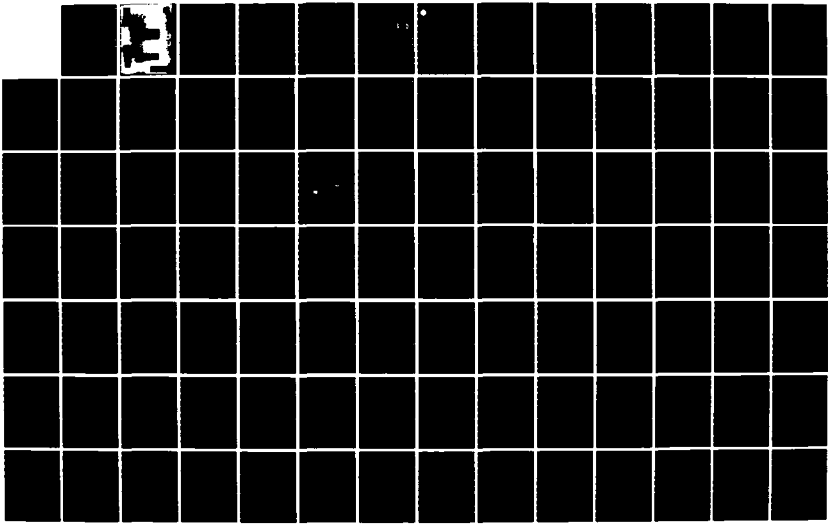

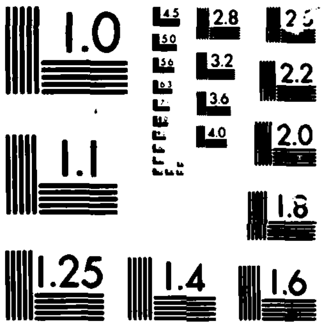

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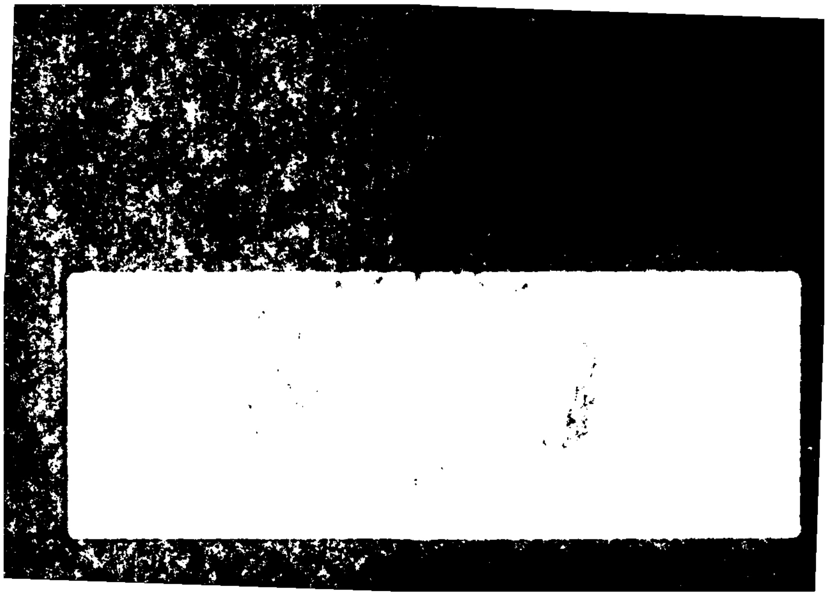

ECONOMIC COMPARISON OF A HIGH PRESSURE CRYSTALLIZATION PROCESS WITH A DISTILLATION PROCESS

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A process capable of a 99+% purity was desired. There exists distillation technology capable of this separation. But, the heat added and removed in a distillation process is very high for a high purity operation and is very expensive. A more energy efficient process is desired by using a high pressure crystallisation process. Crystallization of many systems may result in a complete separation and at theoretical yields. There were two designs examined for high pressure crystallization. The designs differed in the pressurisation of a batch charge. The first was pressurized

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ECONOMIC COMPARISON
OF A HIGH PRESSURE CRYSTALLIZATION PROCESS
WITH A DISTILLATION PROCESS

A Thesis
Submitted to the Faculty

of

Rose-Hulman Institute of Technology

by

James Eric Dietz

In Partial Fulfillment of the
Requirements for the Degree

of

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Graduate Council

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II. FINAL EXAMINATION REPORT

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ABSTRACT

Dietz, James Eric
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January 1986
Economic Comparison of a High Pressure Crystallization
Process with a Distillation Process
Dr. W. W. Bowden

A process capable of a 99+% purity was desired. There exists distillation technology capable of this separation. But, the heat added and removed in a distillation process is very high for a high purity operation and is very expensive. A more energy efficient process is desired by using a high pressure crystallization process. Crystallization of many systems may result in a complete separation and at theoretical yields. There were two designs examined for high pressure crystallization. The designs differed in the pressurization of a batch charge. The first was pressurized by an inert gas. The gas was compressed and fed to the charged crystallizer. The second was hydraulically pressurized. This crystallizer was a double sided piston and cylinder arrangement. The low pressure end had a large piston area and the high pressure end had a smaller area. The pressure difference being the

ratio of the areas. It was found that the hydraulic was least costly, $ 171,300, to build and operate on a 10 year basis. The gas pressurized process was next at $ 180,795. The distillation process, as expected, was most costly at $ 196,200. The gas pressurized process may have more promise to further reduce operating costs. The inert gas could be replaced with air and a diaphragm could be used to separate it for the liquid charge. This would result in an annual savings of $ 4,540 and a savings of $ 6,600 in capital expense. The gas pressurization process is also the process on which a patent would most probably be obtained.

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Nomenclature

A - surface area of heat exchanger
A_1 - surface area of piston 1
A_2 - surface area of piston 2
a - axis of ellipsoid
b - axis of ellipsoid
C_o - feed composition
C_s - solid composition
C_w - waste composition
c - axis of ellipsoid
D - diameter
d - distillate flow rate
E - joint efficiency
e - eutectic point
F - feed flow rate
H - enthalpy
k - separation factor
L_{actual} - actual reflux
L_{min} - minimum reflux
L_{SH} - length of shell
l - liquid waste flow rate
n - moles
P - pressure

P_1 - pure component transition pressure of component 1

P_2 - pure component transition pressure of component 2

P_e - pressure corresponding to the eutectic point, e

Q - heat flow rate

Q_H - heat flow rate for high temperature system

Q_L - heat flow rate for low temperature system

q - flow rate of gas stream

r - radius

R - gas constant

S - maximum allowable pressure

s - product flow rate

T_C - condenser temperature

T_H - high temperature

T_O - ambient temperature

T_L - low temperature

T_R - reboiler temperature

t - thickness of pressure vessel

t - time

U - internal energy

V - volume

V - specific volume

V_{BZ} - specific volume of benzene at P

V_{CH} - specific volume of cyclohexane at P

V_E - volume of ellipsoid

V_H - volume of steel in head

V_o - specific volume at 1 atm

$V_{o\ BZ}$ - specific volume of benzene at 1 atm

$V_{o\ CH}$ - specific volume of cyclohexane at 1 atm

V_{SH} - volume of steel in shell

W_n - net work

X_c - feed composition

X_d - distillate composition

X_e - eutectic composition

X_f - feed composition

X_1 - waste composition

X_{N2} - solubility of nitrogen

X_s - product composition

z - compressibility factor

z - pressure adjustment in ASME design equation

α - relative volatility

λ - latent heat of vaporization

I. Introduction

Crystallization is the formation of solids from solutions or melts. This process may be accomplished in three methods. The first involves separation through a vapor-solid equilibrium. Generally, this involves a solid which is slightly soluble in the gas phase, for example, iodine crystals. The crystals sublime and reform on some new site. This has been called fractional sublimation. Second is a solid-liquid equilibrium process. Commonly, a solid can be purified by dissolving it in a liquid with which it is slightly soluble at room temperature and very soluble at some higher temperature. It is assumed that the impurity present in small quantities is not favored to deposit in the recystallization. This is called recrystallization or solvent recrystallization. The third method is called fractional solidification or melt crystallization. This method works best and is usually used with concentrated systems with an objective of very high purity. The last method is of interest due high recovery and absence of solvent, another contaminant. In the melt, the substance itself acts as the solvent, eliminating the need of a solvent.[28] Melt crystallization usually has the advantage of lower operating costs.

Melt crystallization is not a recent discovery. It was first used during the nineteenth century by whalers. They found that potable water could be obtained from sea ice or icebergs if melted properly.[36] Also by 1918 crude paraffin waxes were separated from petroleum oils exclusively by crystallization. These waxes were further refined by freezing the wax in sheets and placing them over heating coils. Slow melting proceeded, resulting first in the appearance of oil beads which were allowed to run off leaving an even more pure product.[29] The first industrial crystallizer, the Proabd refiner, was developed in 1960. This batch process slowly cooled a charge until solid and then slowly reheated it. The impurities melt and drain first and leave a progressively more pure product.[20] This work will proceed further than the Proabd refiner. It uses high pressure, rather than temperature, as a driving force. The high pressure process will be less costly, while achieving higher purity than a distillation process in use today.

II. Objectives

The stream to be refined has a composition of 90% benzene and a desired product composition of 99+% benzene.

1. Design two high pressure crystallization processes, gas pressurization and hydraulic pressurization, capable of the desired separation.

2. Design a distillation process capable of the desired separation.

3. Compare the three designs on capital investment and on utility costs.

4. Write a Flowtran compatible program to design the crystallizer with gas pressurization.

III. Literature Summary

Crystallization

For discussion of crystallization, there must be several preliminary topics discussed. First nucleation must be discussed to understand the formation of crystals. Next phase diagrams of solid-liquid systems must be understood. Also, for design of a new process, the existing processes must be reviewed. Finally, the energy requirement of each processes must be determined.

Nucleation

Whatever the driving force present, nucleation proceeds in three fundamental steps. The first step demands that the solution obtain some degree of supersaturation or subcooling. Supersaturation is cooling beyond the normal melting point of the system. Supersaturation is not sufficient cause for the development of crystals. Microscopic seeds or nuclei must be present for each successive molecule to deposit. These seeds may be small crystals or any kind of microscopic debris or dust. The third step is the growth of the crystal around the developed centers. Figure 1 will help explain some other terms describing crystallization.[28]

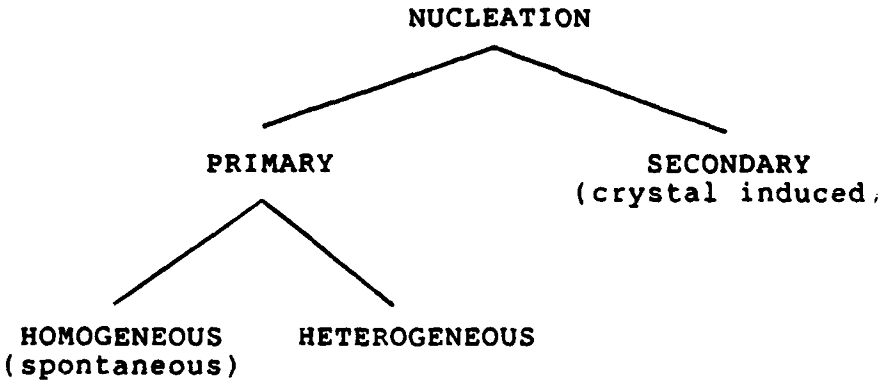

Figure 1. Hierarchy of Crystallization Terms

Most crystals are formed around some sort of dust or debris, heterogeneous nucleation. Most reported cases of spontaneous crystallization are in fact seeded in some manner such as by atmosphereic dust. Normal aqueous solutions contain $10^6 - 10^8$ particles per cubic centimeter.[28] Industrially, crystallization is carried out through heterogeneous or secondary nucleation. Deliberate seeding gives some control over product size and distribution. The rainmaking silver iodide is an example. It has the ability to crystallize water in the atmosphere due to the similarity of the AgI crystal lattice and that of H_2O. Many factors are involved in the ability of a material to seed crystals. Lattice similarity may or may not contribute to the crystallization process.[28]

Phase Diagrams

Knowledge of phase diagrams is required to understand the operation of a crystallizer. The phase diagram is the equilibrium relationship at specified concentration and one other extensive variable (pressure or temperature). This work focuses on the pressure variation.

For discussion, an example of a binary system with eutectic and continuous solid solution will be examined in Figure 2. P_1 and P_2 are pressures corresponding to pure component transition pressures. At these points the liquid, mother liquor, and solid of these pure components are at equilibrium. The point, e, at the intersection of the two curves is called the eutectic point. The two curves go through e due to the effect of subcooling. The pressure increase or supersaturation is required to form crystals. The pressure corresponding to this point is labeled P_e. The solid and liquid at this pressure, P_e, are of the same composition, X_e.

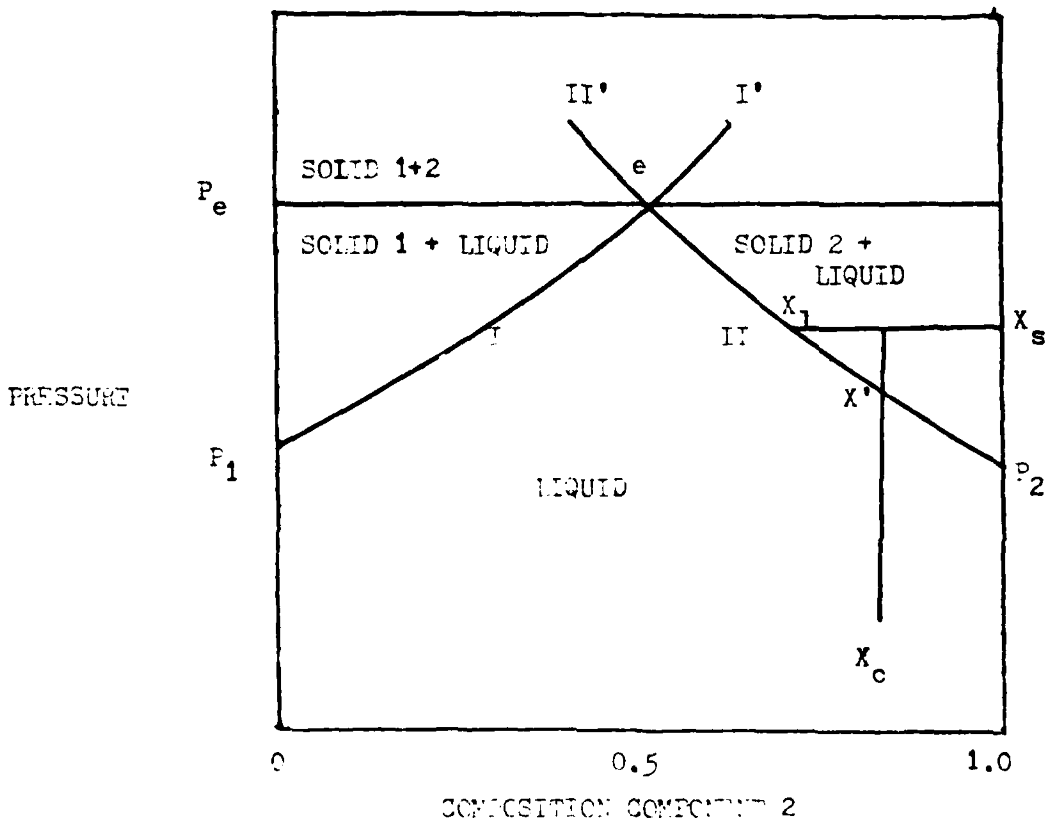

Figure 2. Example of binary system with eutectic and continuous solid solution

Now that the basic points of interest on the phase diagram have been examined, further discussion may proceed on the usefulness of phase diagrams. Assuming a solution of composition X_c, the pressure can be increased to P_c where the first solid component 2 should begin to form. As the amount of solid grows, the concentration of component 1 grows in the mother liquor. At any desired separation, there are two phase concentrations.[37]

Figure 2 can be used to find the relative quantities of solid and liquid using mass balances. This known as the lever rule, involves measuring certain lengths on the graph.

Mass balances

Overall: $F = l + s$ (1)

Component 2: $F \cdot X_c = l \cdot X_l + s \cdot X_s$ (2)

$$F \cdot X_c = l \cdot X_c + (F-l)\, X_c \tag{3}$$

$$l/F = \frac{X_c - X_s}{X_l - X_s} \tag{4}$$

$$l/F = \frac{\text{distance between } X_c \text{ and } X_s}{\text{distance between } X_l \text{ and } X_s} \tag{5}$$

Also:

$$s/F = \frac{\text{distance between } X_l \text{ and } X_c}{\text{distance between } X_l \text{ and } X_s} \tag{6}$$

Binary mixtures to some degree do not crystallize out in pure form. Due to an inconsistent crystal lattice, some impurity may be introduced. The result can be a solid solution. Some are completely miscible but others may have very small solubilities.

There are other relationships in addition those shown on Figure 2 which also must be understood to discuss high pressure crystallization. The first of these is the relationship between pressure and volume decrease under isothermal conditions, Figure 3.

Curve A represents the phase change for the pure liquid material. Crystallization proceeds by compression at constant pressure, A_1 to A_2, beyond A, all material is solid and compression of the solid phase again marks a rise in pressure. The curve B represents the impure material. The difference between A_1 and B_1 is the transition pressure elevation. Like the freezing temperature depression, the pressure difference is a function of the amount of impurity.

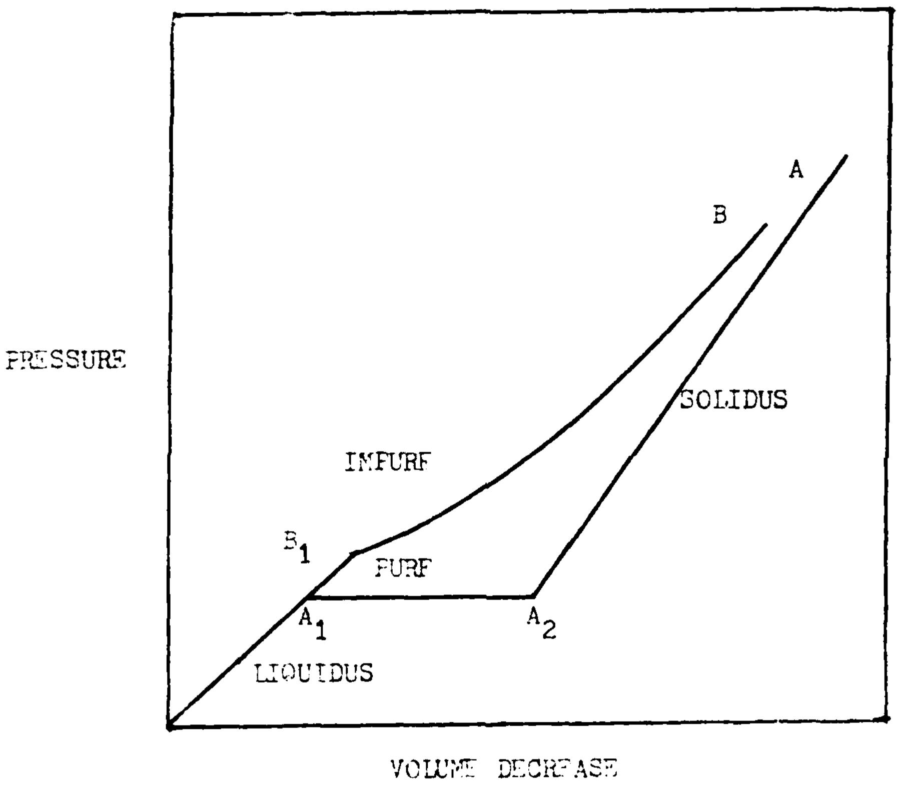

Figure 3. Phase change under pressure of pure (A) an impure (B)

Figure 4 is an example of this for the benzene-cyclohexane system. It is pressure versus fraction of solid, but it is about the same as pressure and volume decrease between A_1 and A_2 . The curve A is 99.5% benzene. The curve B is 100% benzene. Clearly, curve A shows the transition pressure elevation phenomenon.

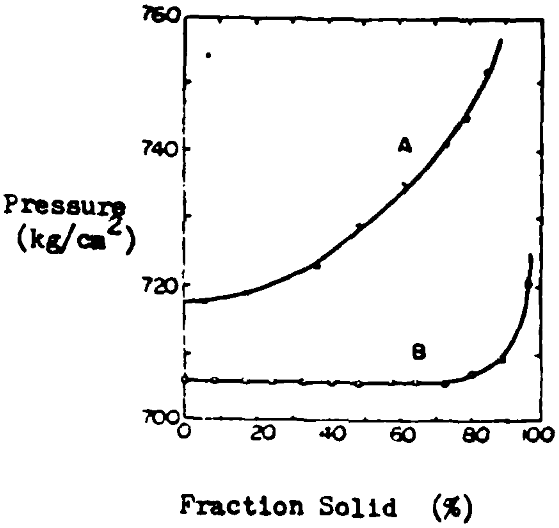

Figure 4. Transition pressure of pure (B) and impure (A) benzene vs. fraction solid [22]

Common Processes

There are two methods to apply the driving force to a crystallization process. The first and perhaps most obvious is to remove heat to drop the temperature. This is the more obvious due to the frequency of occurrence. In most areas ice is a common winter sight. The second driving force is to increase the pressure. It should be known that the freezing point of most liquids increases with the addition of pressure. It should also be realized that the liquid will freeze with the addition of enough pressure.

Common Temperature Processes

With an understanding of phase diagrams, some of the common crystallization processes may be discussed. The first and the simplest is normal freezing. This process slowly freezes the impure mixture to a well defined interface. Freezing proceeds until the desired amount of product is frozen and the remaining mother liquor is discarded. This process is also known as progressive freezing. To identify a progressive freezing process, an interface perpendicular to the longest dimension of the crystallizer will be found.

Gouw[13] attempted to optimize batch normal freezing by using programmed temperature with time. His study found that impurity deposit was not affected early in the freezing cycle. However, late in the cycle, the impurities in the deposited solid could be minimized with the programmed temperature approach. Normal freezing has been used to purify continuous solid solutions.

Fractional melting is another method. It uses slow freezing followed by slow melting. In this process the impurity freezes last and melts first. The impurity remains in concentrated pockets in the melt. The pockets drain to leave a progressively purer solid behind. Glassgow and Ross[12] cite some considerations for use of a fractional melting process. First, the system should segregate simply by cooling. No solid solutions are formed. Second, the system mass should be slowly cooled and reheated close to equilibrium conditions, avoiding any inclusion of the impurity. They recommend use of a closed system to avoid problems involved with handling of toxic, odorous or unstable compounds. They also recommend an adequate driving-force to remove the mother liquor adhering to the crystals. Desirable systems would produce large crystals and have a mother liquor of low viscosity. Aston and Mastrangelo[3], also recognizing these factors, used compressible vanes to squeeze the mother liquor from the crystals and in doing so, reduced the equilibrium time.

The first industrial crystallizer, the Proabd refiner, was originally used to purify napthene. Economics of an industrial process are very important and equilibrium is traded for productivity. The separation factor obtained, K, will be less than that which could be achieved by equilibrium. For supervision and labor requirements to be minimized, the process is operated in long cycles which vary from 24 - 48 hours. Half of this time is used for cooling, the remaining half for warming, draining and refilling. The crystallizer is a large container with a heat exchange network capable of uniform heat transfer. The flow rate of the heat exchange medium is kept high to maintain a small temperature difference, .5° C, and uniform conditions.[20]

The product liquid, when drained, will be of varying composition. Many fractions could be removed, however, for practical considerations only three are removed. The mother liquor is the first removed and is later discarded or recycled to a unit process before the crystallizer. The second is a crystallizer recycle, usually of purity equal to, or greater than that of the feed. The final fraction is the pure product fraction.[20]

Common Pressure Processes

It is obvious that heat transfer problems must be solved to operate the Proabd refiner, however, this paper is concerned with the pressure driven, adiabatic, crystallization process. There are two methods to be considered to carry out the crystallization. The first is a gas pressurized process. The idea with this method is to use the gas to apply the work and crystallize the liquid. This is desirable due to the low cost of the crystallizer. There would be no working parts or piston. The use of a reciprocating compressor would introduce more cost but perhaps less than the large piston of the second process. There is no known process which is operated in this manner. The second method is hydraulic. A large piston at low pressure drives a smaller piston in the crystallizer. Working in this manner, M. Moritoki and co-workers have developed a pilot plant capable of producing industrial quantities.[25] Their process is adiabatically pressurized which is accompanied by a temperature rise. This Kobe Steel group found that the initial state and increase in pressure would determine the temperature, solid fraction and mother liquor concentration. Figure 5 is a diagram of the process.[18]

This process operates in five steps. Figure 6 is a pressure-temperature diagram of operation of the process. First, A, the piston is raised to introduce the feed followed by the second step, B - C, the adiabatic pressurization. Third, C - D, the liquor is removed by filtering through a mesh. The fourth step, D - E, is the compaction and sweating of the crystals still under pressure. This step reduces the pressure to allow the crystals to melt and wash the liquor from the surfaces. Finally, the compressed, washed cake is removed if solid or drained if liquid.[18]

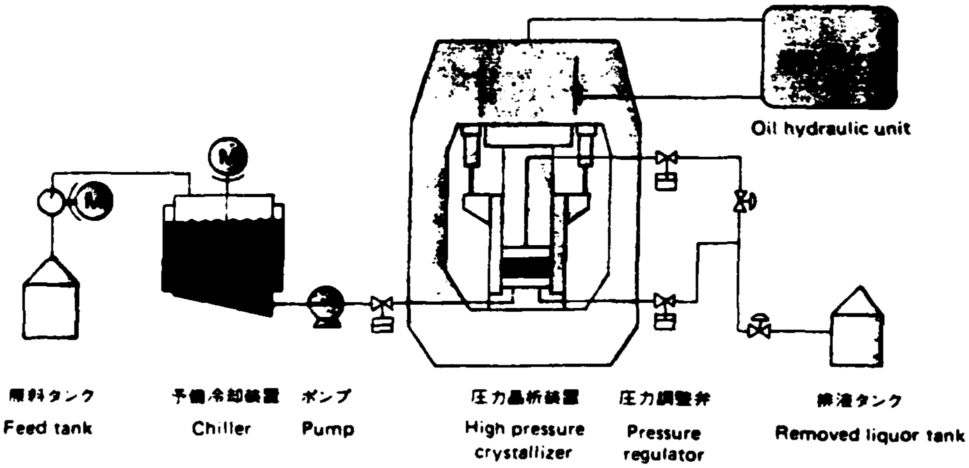

Figure 5. Diagram of Kobe Steel High Pressure Crystallization Process [25]

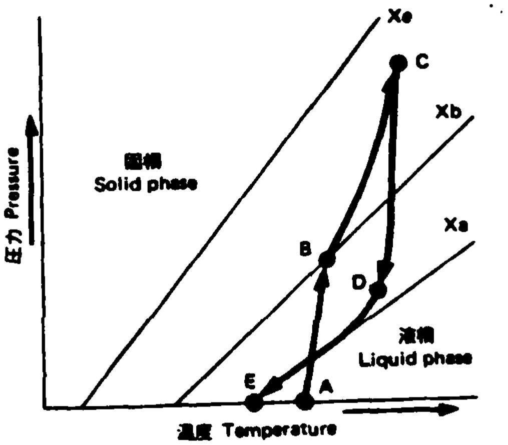

Figure 6. Pressure-Temperature relationship for Kobe Steel adiabatic crystallization process [25]

a- equilibrium line of pure substance

b- equilibrium line for initial concentration

c- equilibrium line for eutectic concentration

After many trials, Moritoki and co-workers at Kobe Steel concluded that the distribution coefficient could be reduced with increasing pressure. At each pressure-temperature pair a distribution coefficient is obtained. From this coefficient an exit concentration can be calculated and is reported. For the benzene - cyclohexane system, Figure 7 was reported.[22]

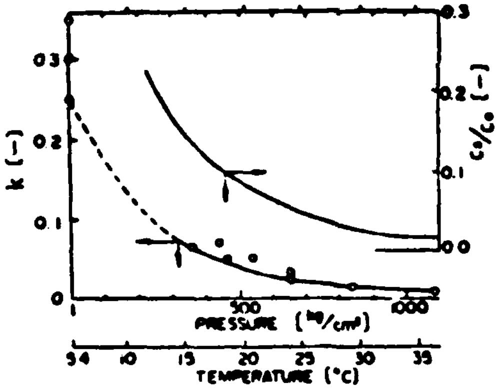

Figure 7. Relationship of k and C_s/C_o to operating conditions for benzene-cyclohexane system[22]

Systems under high pressure are subject to a second desirable effect. The eutectic has a tendency to move right, as in Figure 8. With increasing pressure, this allows for a greater possible theoretical separation.[23]

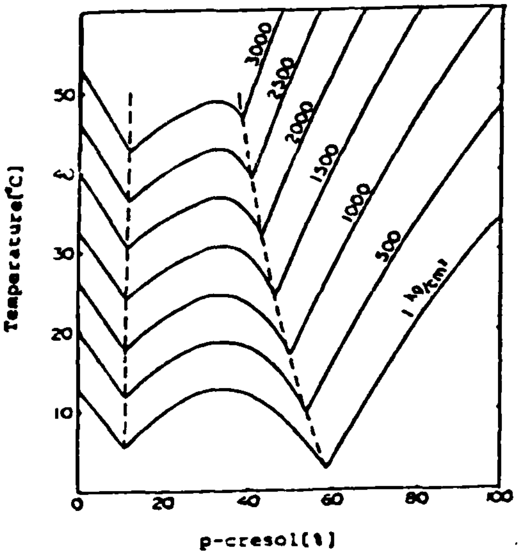

Figure 8. Phase diagram of m- and p-cresol [23]

The experimental values of the Kobe Steel group indicated that 90 - 100% of the theoretical yields could be obtained. Since this is a pressure change operation, several operations may be simply and rapidly carried out.

Pressure is rather uniform throughout the crystallizer and the operating cycle. This is the major factor which reduces the minimum operating cycle time and uniform impurity distribution.

Distillation

The purpose of this work is to economically compare a design for a high pressure crystallization to distillation. So a brief discussion of distillation is warranted.

Distillation is defined as the process of producing vapor from a liquid in a vessel and collecting and condensing the vapors into liquids. This is done in many steps with each step progressively purer. The separating agent in distillation is heat and separation is based on differences in vapor pressures or boiling points. The following is an example of the vapor-liquid equilibrium necessary to study distillation. Figure 9 is an example of the vapor-liquid equilibrium relationship with a McCabe-Thiele diagram. As seen in Figure 9, the higher the desired purity the greater the number of stages required. This side of the phase diagram, separation at high purity is referred to as a pinch point.

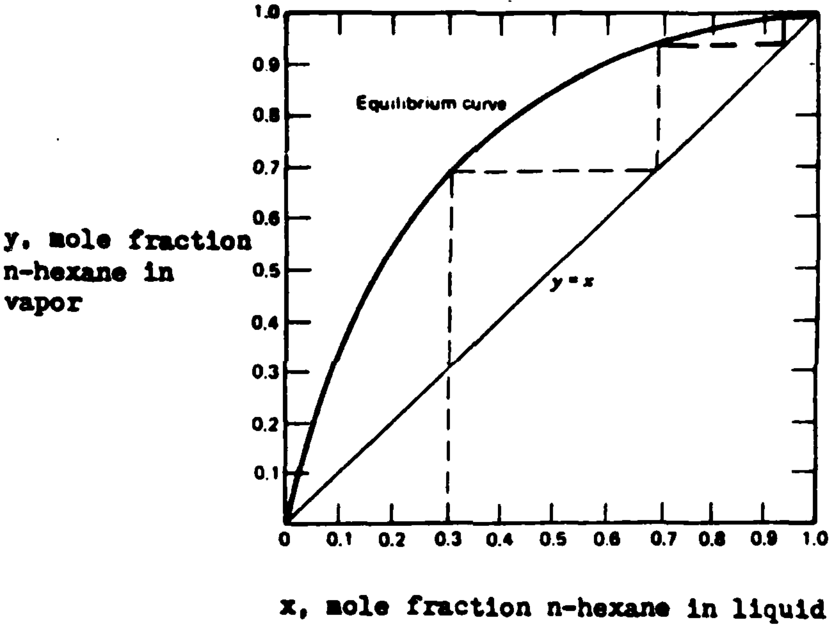

Figure 9. Vapor-liquid phase diagram for illustration.[30]

As illustrated in Figure 9, high increases in purity can be realized by distillation in the middle range but as an increasingly pure liquid is fed in each stage a lower increase in purity is realized. An increasing number of stages are required to obtain a product more than 99% pure. The result is a much higher energy cost.

Minimum Work

In an economic comparison, energy costs are also important. The minimum energy of separation related to the each process is different. The minimum work of each process is needed to compare. First distillation is studied. Then the minimum work applying to the high pressure process is examined.

Minimum Work of Distillation

King[17] classifies distillation as a potentially reversible process. That can be viewed similarly to a heat engine. The column operates by taking in heat and producing a separation. Then, the reversible heat entering would be:

$$Q_H \, (T_H - T_O)/T_O \qquad (7)$$

The heat leaving would be:

$$Q_L \ (T_L - T_O)/T_L \tag{8}$$

Q_H - Heat entering the high temperature engine
Q_L - Heat entering the low temperature engine
T_H - High temperature
T_L - Low temperature
T_O - Reservoir temperature

The net work would be the difference between the heat entering and the heat leaving the system.

$$W_n = Q_H \ (T_H - T_O)/T_H \ - \ Q_L \ (T_L - T_O)/T_L \tag{9}$$

Assuming no mechanical work, the energy differences between the product and feed will be small. The heat flows reduce to:

$$Q_H = Q_L = Q \tag{10}$$

and equation (9) simplifies to:

$$W_n = Q \ T_O \ (1/T_L - 1/T_H) \tag{11}$$

If the condenser is considered the low temperature region and the reboiler considered the high temperature region, then equation (11) becomes:

$$W_n = Q_C \ T_O \ (1/T_C - 1/T_R) \tag{12}$$

Q_C is determined by using minimum reflux:[17]

$L_{min} =$ [illegible] (13)

Also, when [illegible] the minimum reflux reaches an [illegible].

$L_{min} =$ [illegible] (14)

λ is the latent heat of vaporization.

$$Q_C = \lambda (L_{min} + d) \tag{15}$$

$$d/f = X_f. \tag{16}$$

Also for a close boiling mixture $L_{min} > d$. This and combining (15) and (16) leads to:

$$Q_C = \lambda /(\alpha - 1) \quad F \tag{17}$$

α and λ can be determined using the Clausius - Clapeyron equation:[8]

$$\frac{d \ln P}{d\ 1/T} = - \frac{\lambda}{R} \tag{18}$$

The overhead temperature, T_c, for a component in a complete separation is close to the boiling point of that component at the column pressure. Likewise, T_r is close to the boiling point of the less volatile component. The vapor pressure of the more volatile component at the bottoms temperature would be α times the column pressure. By integrating the Clapeyron equation, the result is:

$$\ln \alpha = \lambda /R \quad (1/T_C - 1/T_R) \tag{19}$$

With the assumption of an α close to 1 , or a close boiling mixture, $\ln \alpha$ equals $\alpha - 1$. The α for the benzene-cyclohexane system is 1.059 at 0°C, 1.027 at 25°C, and 1.003 at 50°C. The is some temperature dependence but the assumption of α close to 1 remains valid.

The assumption of and by combining (11), (17) and (19):

$$W_n = R\ F\ T_o \tag{20}$$

For any reflux above minimum, the equation would be increased by a factor of actual vapor rate divided by minimum vapor rate:

$$\begin{aligned} W_n &= \text{(Actual vapor rate)/(Minimum vapor rate) } R\ F\ T_o \\ &= (L_{Actual} + d)/(L_{min} + d)\ \ R\ F\ T_o \end{aligned}$$

Minimum Work of Pressurization

The minimum work for the pressurization process is much simpler. If the assumption is made that the compression is done adiabatically, reversibly, the solid is pure, and all solid is recovered as pure product, then the minimum work is:

$$W = \int_1^2 P\ dV \tag{21}$$

Given an equation of state for the solution, the work can easily be calculated.

IV. Design of Process

To do a specific comparison of distillation to high pressure crystallization, a material or system must be chosen. Benzene of 90% and cyclohexane of 10% were used. Benzene is an important building block for styrene or phenol in many modern synthetic fiber and resin processes.[19] Now that a system is chosen, the production rate must be determined. Presently, several conventional benzene production plants are under construction worldwide. These plants are designed for annual production rates between 10^5 and 10^8 Kg/year.[16] Also, Chaty[6] compares various industrial processes where the annual flow rates for benzene production are 10^6-10^7 Kg/year.[6] With these data, an annual production rate of $1\text{x}10^6$ Kg/year was chosen.

The third decision is to determine a reasonable cycle time for the high pressure crystallization. Mortiki and co-workers[25] indicate a minimum cycle time for their process of 2 minutes, allowing 10 seconds for pressurization and equilibrium, 40 seconds for filtration and the remaining time for sweating and compacting.

Correspondence with Mr. Mortiki suggests a time of several minutes. The absence of data, and the decision to use an inert gas for the compression, required a high estimate of 30 minutes per cycle.

A phase diagram for this system is also necessary. Figure 10 is the phase diagram for the benzene-cyclohexane system.

Finally, an initial temperature of 25° C was selected for the adiabatic process.

Crystallizer Design with Gas Pressurization

A basis has been completed so the process equipment may now be sized. The separation of the cyclohexane is first determined. Moritoki published a relationship of solid phase concentration to initial concentration for the impurity, Figure 7.[22]

At 25° C, the C_s/C_o is found to be .027, which corresponds to a product of 99.7% benzene.

An outlet concentration must be selected for the mother liquor. There is an optimum between increase in pressure and reduction in waste. The outlet concentration was selected to be 75% benzene, corresponding to a maximum pressure of 1400 Kg/cm^2, as seen in Figure 10.[18] Assuming 8,000 hours of operation and 16,000 cycles per year, the product rate per cycle is 62.5 Kg or 137.75 lbs.

Thus far, no specifics about the process have been discussed and the process layout need not be known.

The crystallizer is central to the design. The means by which to increase the pressure must also be provided. Therefore, a compressor, followed by a heat exchanger, will be necessary. The crystallizer feed stream may also need to be precooled to remove the heats of compression and fusion. Hence, the flow diagram would be Figure 11. The crystallizer is shown in Figure 12.

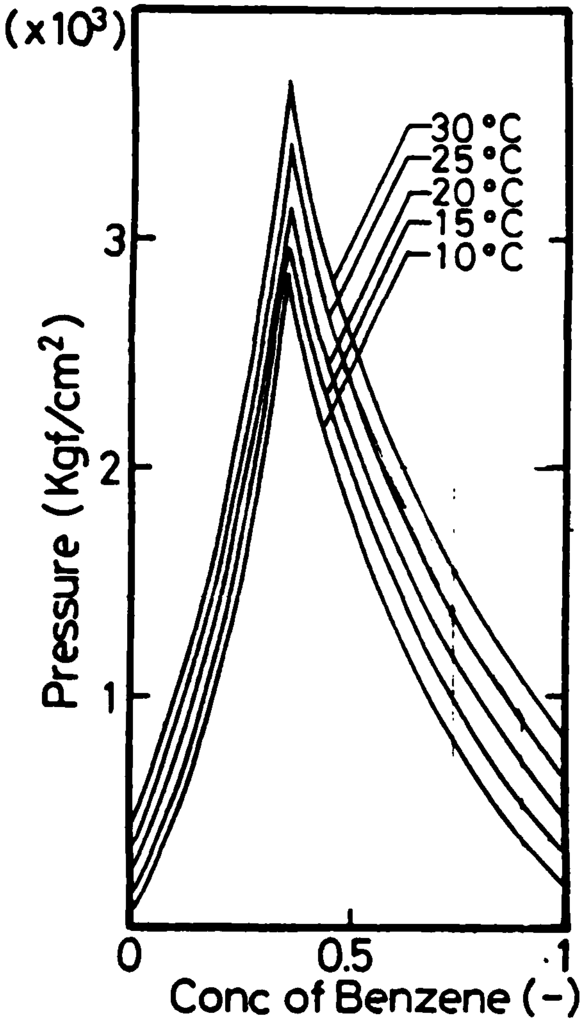

Figure 10. Phase diagram for benzene-cyclohexane system [26]

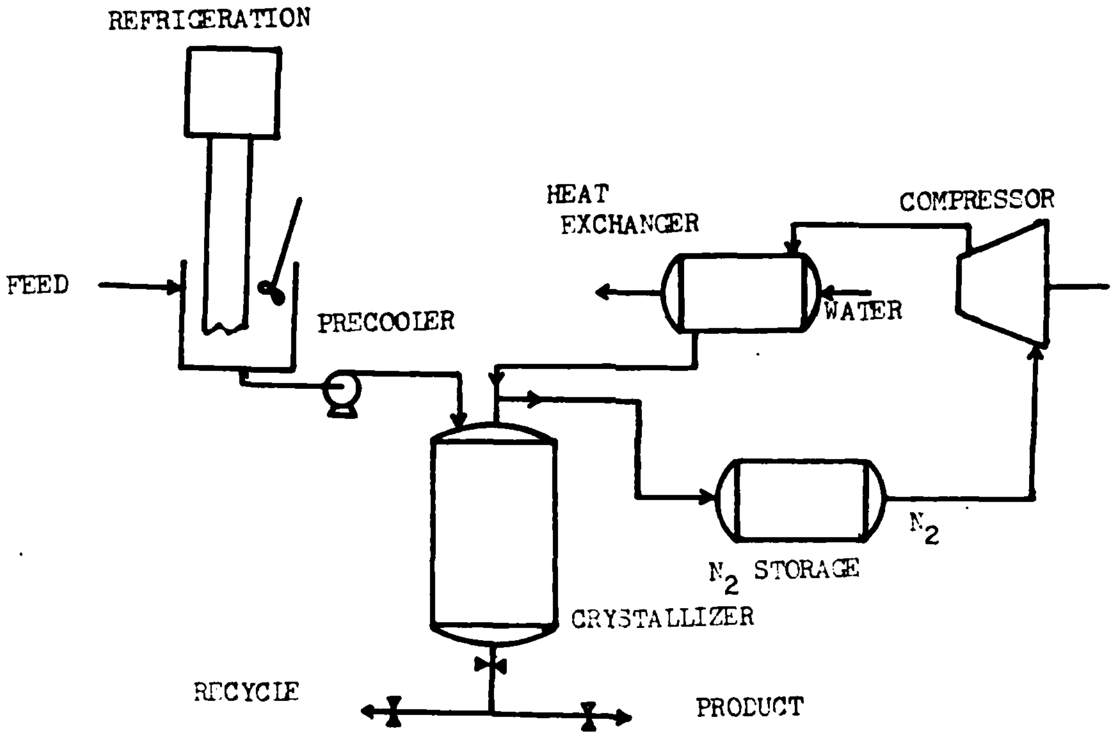

Figure 11. Flow diagram for gas pressurized crystallization process

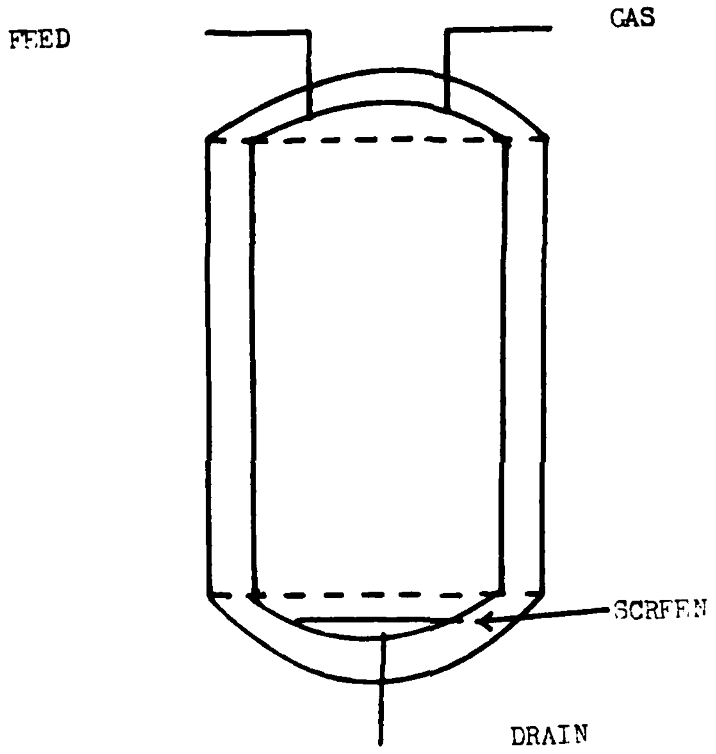

Figure 12. Crystallizer for gas pressurization process

Mass Balance

Knowing concentrations in all streams and the product flow rate, a mass balance may be completed on the crystallizer loop.

$$C_s = .002$$
$$C_o = .1$$
$$C_w = .25$$

$$\text{Product} = 62.5 \text{ Kg/cycle}$$

$$\text{Total Mass:} \quad \text{Feed} = \text{Product} + \text{Waste} \qquad (22)$$
$$\text{Cyclohexane Mass:} \ C_o \cdot \text{Feed} = C_s \cdot \text{Product} + C_w \cdot \text{Waste} \quad (23)$$

$$(.1)(\text{Feed}) = (.002)(62.5) + (.25)(\text{Waste})$$

by solving (22) and (23).

$$\text{Feed} = 102.9 \text{ Kg/cycle}$$
$$\text{Waste} = 40.4 \text{ Kg/cycle}$$

Crystallizer Volume at P_o

At atmospheric pressure, the feed volume is known and the system volume can be calculated.

$$\text{Volume} = (M_{BZ})(V_{BZ}) + (M_{CH})(V_{CH}) \qquad (24)$$

$$V_{BZ} = 1.138 \text{ cm}^3/\text{gm}$$

$$V_{CH} = 1.284 \text{cm}^3/\text{gm}$$

$$\text{Volume} = (102.9)(.9)(1.138) + (102.9)(.1)(1.284)$$

$$\text{Volume} = 118.62 \text{ L}$$

Crystallizer Volume at P

For benzene, Gehrig and Lentz[9] report a modified Tait equation for P in MPa:

$$\frac{V_o - V}{V} = A \quad \ln \frac{(B + P)}{(B + P_o)} \qquad (25)$$

In the 25^o C range:

A = .1845
B = 194.5 MPa.

For cyclohexane, another version of the Tait equation is reported for P in Kp/cm^2:[33]

$$\frac{V_o - V}{V_o} = C \log \frac{B + P}{B} \qquad (26)$$

In the 25^o C range:

C = .2272
B = 723.3 Kp/cm^2 .

P is 1400 Kg/cm^2 at 25^o C and 75% benzene. Also, P_o is 1 atm and the V_o's are:

$V_{o\ BZ}$ = 1.138 cm^3/gm
$V_{o\ CH}$ = 1.284 cm^3/gm

Each equation of state uses different units of pressure.

P =1400 kg/cm^2 =137.0 MPa =1350 atm =1395 kp/cm^2

$$\frac{V_{o\ BZ} - V_{1\ BZ}}{V_{1\ BZ}} = .1845 \ln \frac{194.5 + 137.0}{194.5 + .101}$$

$$V_{1\ BZ} = 1.036 \text{ cm}^3/\text{gm}$$

From Bridgman[5], the change in volume of solid benzene $\Delta V/V_o$ is .0902.[5]

$$\frac{\Delta V}{V_o} = \frac{V_o - V}{V_o} = .0902$$

$$V_{s\ BZ} = .943\ \mathrm{cm}^3/\mathrm{gm}$$

$$\frac{V_{o\ CH} - V_{1\ CH}}{V_{o\ CH}} = .2272 \ln \frac{920 + 1395}{920}$$

$$V_{1\ CH} = 1.167\ \mathrm{cm}^3/\mathrm{gm}$$

At the maximum pressure, the volume will be composed of the product amount of solid and the liquid quantity of waste.

Volume = solid benzene + liquid benzene + liquid cyclohexane

$$\begin{aligned}\text{Volume} &= (167.5)(.943) + (40.4)(1.036) + (40.4)(.25)(1.167)\\ &= 102.1\ \mathrm{L}\end{aligned}$$

Liquid Volume = 43.2 L

Nitrogen Needed

The volume decrease between P and P_o can now be calculated and the amount of liquid is known. The amount of nitrogen needed to be compressed is calculable. This solubility data on Nitrogen in benzene is available at 120 atm and 25° C.[11] It is understood that the operating pressure of the system is much higher. But, at the highest pressure the system would be mostly solid. The solubility of nitrogen in the solid would be small. These data will be assumed close for this liquid system.

$$X_{N2} = .0551 \text{ mole fraction}$$
$$= .02050 \text{ mass fraction}$$

So, the nitrogen dissolved is:

$$\text{mass solution} = (.02050)(40.4)$$
$$= .828 \text{ Kg}$$

$$\Delta V = 118.6 - 102.2$$
$$= 16.5 \text{ L}$$

$$P \Delta V = ZnRT$$

$$P_r = 40.3$$

$$T_r = 2.36$$

$$Z = 2.2$$

$$(1350)(16.51) = (2.2)\ n\ (82.06)(298)$$

$$n = .4140 \text{ Kg mole}$$
$$= 11.59 \text{ Kg}$$

Total mass nitrogen = 12.68 Kg

Due to the assumed solubility this may be a high estimate.

The volume (SCF) of gas can also be calculated:

$$(1)\ V = (.4530)(.7306)(637)$$
$$= 463 \text{ SCF}$$

Pressure Vessel Design

The crystallizer, a high pressure vessel, has a large number of regulations involved with its design. The American Society of Mechanical Engineers, (ASME), have established rules and standards governing safety, design, fabrication and inspection.[1] The desired vessel is a cylindrical shell with a 50 cm ID and 2:1 ellipsoidal heads. The maximum pressure is 19,700 psi and material of construction is A-302B with an allowable stress of 26,500 psi.[1] All joints will be fully radiographed in accordance with UW-11(a), Reference 1. The joint efficiency is 1.0 when joints are fully radiographed.

Shell circumferential stress is calculated for thick cylindrical shells from Appendix 1,1-2(a)(1), Reference 1.

$$t = R\,(Z^{.5} - 1) \qquad (29)$$

$$Z = \frac{S \times E + P}{S \times E - P} \qquad (30)$$

$$t = (25)\left[\frac{(26500 + 19700)}{(26500 - 19700)}\right]^{.5} - 1$$

$$= 40.2 \text{ cm}$$

Shell longitudinal stress is also calculated for thick cylindrical shells in accordance with Appendix 1, 1-2(a)(2), Reference 1.

$$t = R\ (Z^{.5} - 1) \qquad (31)$$

$$Z = (P/(S \times E) + 1) \qquad (32)$$

$$t = (25)((19700/26500 + 1)^{.5} - 1)$$

$$= 8.01 \text{ cm}$$

The largest of the two values is used. The shell thickness would be 40.2 cm. The heads are to be 2:1 ellipsoidal in accordance with UG-32(d), Reference 1.

$$t = \frac{P \times D}{2\ S \times E - .2\ P} \qquad (33)$$

$$= \frac{(19700)(50)}{(2)(26500)(1)-(.2)(19700)}$$

$$= 20.07 \text{ cm}$$

To proceed further in sizing the crystallizer the length of the vessel must be determined. This is found by subtracting the volume if the heads from the total volume needed and dividing that difference by the crystallizer cross-sectional area. Once the length is known, an approximate volume of the construction material of can be found. Since pressure vessels are roughly priced by total weight, these calculations will complete the cost.

$$V_E = 4/3 \pi a b c \qquad (34)$$

The variables a, b, and c are the lengths of the semi-axies.

$$V_E = (4/3) \pi (25) (25) (12.5)/(1000)$$
$$= 32.7 \text{ l}$$

$$V_S = 135.3 - (2)(32.7)$$
$$= 69.9 \text{ l}$$

$$L_S = V_S / \pi R^2$$
$$= (69900)/ \pi (25)^2$$
$$= 35.6 \text{ cm}$$

The volume of building material of the shell and the heads must be determined. The volumes calculated using the outside radius are subtracted from the volume inside radius.

$$V_{MS} = \pi L ((R+t_S) - R) \qquad (35)$$
$$= 35.6 ((25+ 40.2) - 25)$$
$$= 4.053 \times 10^5 \text{ cm}^3$$

$$V_{MH} = (4/3) \pi ((a+t_H)(b+t_H)(c+t_H)-abc) \qquad (36)$$
$$= (4/3) \pi ((45.1)(45.1)(32.6)-25^2 12.5)$$
$$= 2.778 \times 10^5 \text{ cm}^3$$

$$V_{total} = 9.609 \times 10^5 \text{ cm}^3$$
$$= .29 \text{ lb/in}^3$$
$$= 1.77 \times 10^{-2} \text{ lb/cm}^3$$

$$\text{Mass} = 1.204 \times 10^4 \text{ lb}$$

Applying data from Figure 6, Reference 6, the cost per pound would be \$ 1.20 and an additional \$ .60 for stainless steel construction.

Total cost = \$ 21,700

Minimum Work

Finally, the minimum work for the compression of the liquid mixture must be calculated. This calculation, as stated earlier, is simply the integral of PdV. The work is calculated in 3 parts.

The integrals of PdV for liquid benzene and liquid cyclohexane are summed over each range of specific volume. The integral of PdV is also calculated for the transition of benzene from liquid to solid and the compression of the solid. The following equations are used;

for liquid benzene:[9]

$$\frac{V_o - V}{V} = A \ln \frac{B + P}{B + P_o} \qquad (25)$$

for liquid cyclohexane:[33]

$$\frac{V_o - V}{V_o} = C \log \frac{B + P}{B} \qquad (26)$$

The benzene liquid - solid transition is known. Data from Bridgman for solid benzene was developed into the line for the P-V relationship over the interval $680 < P < 1500$ kp/cm^2.[5]

$$P = 101,500 \ (V_o - V)/V_o - 15,520 \qquad (37)$$

For illustration, large step sizes will be used. More reasonable steps are used with a design program to be used with Flowtran, only a few points are reported and graphed. Data was only available for one point between the pressure of initial crystallization and the highest pressure achieved. These data give the line above.

Table 1
Results of Work Done on Liquid Components

Pressure (Kg/cm^2)	Pressure average (atm)	Benzene ΔV (L/Kg) 10^{-3}	Benzene Pave ΔV (atm L/Kg)	Cyclohexane ΔV (L/Kg) 10^{-3}	Cyclohexane Pave ΔV (atm L/Kg)
1					
100	49.0	1.000	.5	1.273	.6
200	145.6	.920	1.3	1.152	1.7
300	242.7	.855	2.1	1.068	2.6
400	339.8	.805	2.7	.967	3.3
500	436.9	.745	3.3	.908	4.0
600	534.0	.700	3.7	.845	4.5
700	631.1	.655	4.2	.790	5.0
Total work per kilogram (atm L/Kg)			17.8		
800	728.2	1.88	13.7	.748	5.4
900	825.2	.66	5.4	.707	5.8
1000	922.3	.63	5.8	.673	6.2
1100	1019.4	.61	6.2	.629	6.4
1200	1116.5	.58	6.5	.605	6.7
1300	1213.6	.55	6.7	.573	7.0
1350	1286.4	.27	3.5	.280	3.6
Total work per pound (atm L/Kg)			65.6		62.9

Table 2
Results of Work Done on Solid Benzene

Pressure (Kg/cm^2)	Pressure (average) (atm)	ΔV_{TRANS}	V (L/Kg)	ΔV	Pave ΔV	PaveΔV_{TRANS} (atm L/Kg)
680		.1596	1.045			
1400	1003	.1794	1.051	.00494	4.95	179.9
2500		.1992	1.058			
Total work per pound (atm L/Kg)						184.9

These totals can be multiplied by the quantity of each component of the mixture to give an estimate of the work required for the compression.

$$\begin{aligned}\text{Work} &= \text{Solid Benzene} + \text{Liquid Benzene} \\ &\quad + \text{Liquid Cyclohexane} \qquad (38) \\ &= (184.9)(62.5) + (65.6)(30.2) + (17.8)(62.5) \\ &\quad + (62.9)(10.3) \\ &= 15{,}300 \text{ L atm} \\ &= 1500 \text{ BTU} \\ &= 10.25 \text{ BTU/Kg}\end{aligned}$$

Tables 1 and 2 give reasonable estimates for the work required. A more accurate model was constructed by writing a FORTRAN program to do the above calculations. Table 3 gives the result of that program and Figure 13 graphically shows the pressure-temperature relationship.

Table 3
Work on Benzene-Cyclohexane System

Pressure(atm)	Work(BTU)		Temperature
	Cycle	lb Product	Difference(°F)
23.6	7	.1	.1
158.9	75	.6	.8
294.2	174	1.3	1.9
429.5	286	2.1	3.2
564.9	405	2.9	4.5
700.2	524	3.8	5.8
835.5	645	4.7	7.1
970.9	765	5.6	8.5
1016.0	862	6.3	9.5
1061.1	961	7.0	10.6
1106.2	1044	7.6	11.6
1151.3	1116	8.1	12.4
1196.4	1180	8.6	13.1
1241.5	1238	9.0	13.7
1286.6	1291	9.4	14.3
1331.7	1407	10.2	16.7

Precooler

From the data it is clear that the heat of compression (work) and heat of fusion must be removed. This will allow the system to crystallize at the desired temperature of 25 °C. A cooler must be designed to remove 1407 BTU per operating cycle. Again, an overall heat transfer coefficient of 26 BTU/lbmol ft^2 °F will be used. The temperature difference will be 20 °F. This will be carried out in a stirred jacketed tank.

This process needs some means of cooling the feed stream by removing 1407 BTU in 2/3 of a cycle. A

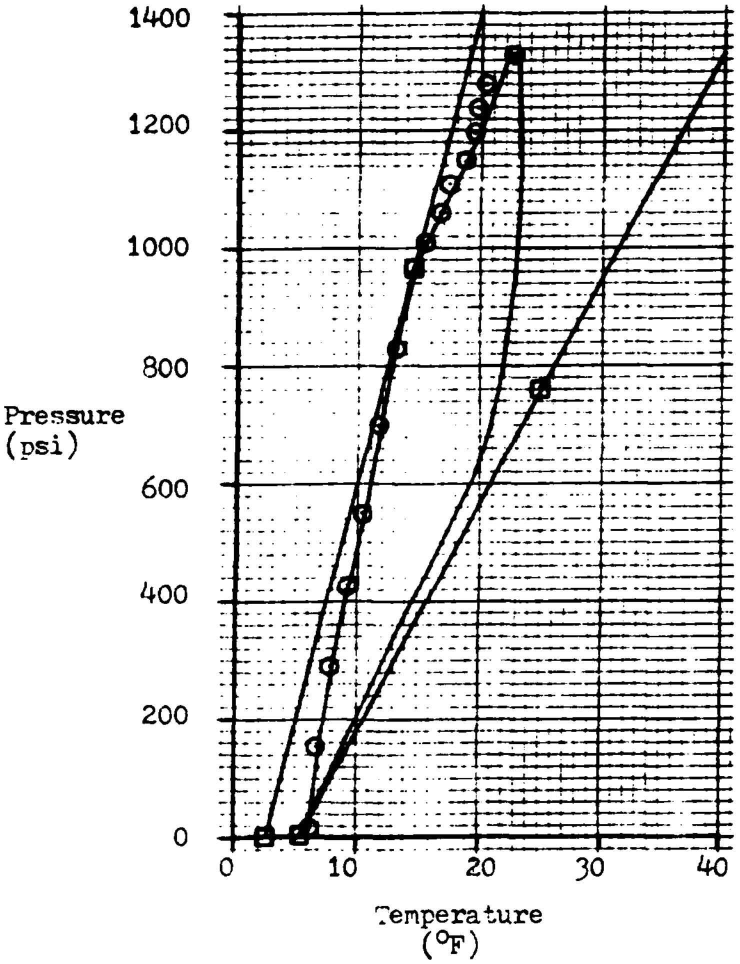

Figure 13. Pressure-temperature relationship for benzene-cyclohexane system.

```
HIGH PRESSURE CRYSTALLIZER
BLOCK - BHPC      NAME - CRYS
OPERATING PRESSURE = 1354.292ATM
CRYSTALLIZER VOLUME =  117.779L
SPECIFIC VOLUME OF BENZENE [cc/g]
LIQUID AT PO 1.13800           LIQUID AT P 1.05327
SOLID AT P 0.95638
SPECIFIC VOLUME OF N-HEXANE [cc/g]
LIQUID AT PO =  1.28400           LIQUID AT P =  1.16857
SHELL THICKNESS[IN]=15.55492SHELL MASS[LB]=        8693.15
HEAD THICKNESS[IN]= 7.83211HEAD MASS[LB]=        3954.87
CRYSTALLIZER COST = $  22766.44
MINIMUM WORK PER HOUR =      2815.598BTU
MINIMUM WORK PER POUND PRODUCT   9.483
NITROGEN DISTRIBUTION [LB]
IN SOLUTION =      6.60IN GAS PHASE =     23.37
CONCENTRATION OF IMPURITY (N-HEXANE)
IN = 0.097414PRODUCT = 0.001656MOTHER LIQUOR = 0.750000
```

Figure 14. Flowtran output for gas pressurized system

refrigeration plant of .40 ton-day capacity would be sufficient. Figure 13-81, Reference 30, has data on NH_3 refrigeration plants. The ammonia expansion is assumed at constant temperature so the assumed temperature difference is tolerable. A system capable of 10 ton-day would cost \$ 17,000.

Refrigeration Plant

$$\text{Cost} = 17{,}000\,(.40/10)^{.6}$$
$$= \$\ 2{,}500$$

Heat Transfer

$$A = \Delta H / U \Delta T \qquad (39)$$
$$= (1407)(6)/(26)(20)$$
$$= 15.8\ \text{ft}^2$$

Cost for heat transfer area[30] = \$1700

The volume of the tank should equal that of the crystallizer, 40 gallons.

Cost mixed tank[30] = \$4000 for 100 gallons

$$\text{Cost} = 4000\,(40/100)^{.6}$$
$$= \$2300$$

Total Precooler Unit Cost = \$ 6,500

Compressor and Heat Exchanger

The gas compressor must be specified. A multi-stage compressor should be used since the outlet pressure exceeds the inlet pressure by more than 5 times. A single stage reciprocating compressor will be used, because, a small volume of gas is to be compressed.

First, the gas flow rate must be calculated. The compression will be 10 minutes of the 30 minute cycle time for each crystallization cycle.

$$q = V/t = ZnRT/Pt \tag{40}$$

$$= \frac{(2.2)(.4140)(82.06)(298)}{(10)(13.6)}$$

$$= 74.39 \text{ L/min}$$

$$= 2.627 \text{ ft}^3\text{/min}$$

The appropriate equation to determine the power requirement is the first law of thermodynamics.[4]

$$Q - W_n = U_2 - U_1 - \int h_{IN} \cdot dm \tag{41}$$

The system is adiabatic and the values of enthalpy are found in data on nitrogen. [2]

$$U = H - P \cdot V \tag{42}$$

The first law simplifies to:

$$-W_n = (H_2 - P_2 \cdot V_2) - (H_1 - P_1 \cdot V_1) - H_1 \cdot \Delta m \quad (43)$$

$$-W_n = (6316-(150)(51.88)) - ((-38)-(1.5)(1659)) - (38)(453)$$

$$-W_n = 448.3 \text{ BTU/cycle}$$

The minimum work the compressor must do is the sum of the minimum work on the liquid and the minimum work on the nitrogen gas. This sum multiplied by a 72% effiency for the compressor and divided by the time the compressor operated would give an approximate power requirement for the compressor motor.

$$\begin{aligned} -W_n &= \text{Work on Gas} + \text{Work on Liquid} \quad (44)\\ &= 448.3 + 1407\\ &= 1855 \text{ BTU} \end{aligned}$$

$$\begin{aligned} \text{Power} &= 1855/(.72)(600)\\ &= 6.07 \text{ hp} \end{aligned}$$

Also with similar data on nitrogen,[2] the outlet temperature can be calculated.

$$\begin{aligned} \Delta H &= (H_2 - H_1)/E \quad (45)\\ &= C_p dT \quad (46)\\ H_2 &= 6316 \text{ J/gmol}\\ H_1 &= 38 \text{ J/gmol}\\ C_p &= 35.0 \text{ J/gmol}\cdot {}^oK\\ \Delta T &= (6316-38)/(32.0)(.72)\\ \Delta T &= 195\ {}^oC\\ &= 382\ {}^oF \end{aligned}$$

The compressor is sized by a correlation of cost vs power.[30] The required power is lower than any graphed, so a cost size extrapolation factor is used.

For 100 hp, the cost of the unit is $30,000 at 5000 psi.[14] This must be extrapolated to 8.1 hp and 20,000 psi discharge.

$$\begin{aligned} \text{Cost} &= 30{,}000\ (6.1/100)^{0.8}\ (20{,}000/5{,}000)^{0.8} \\ &= \$\ 9{,}700 \end{aligned}$$

The heat exchanger may be designed knowing the compressor design, the heat capacity of nitrogen and the outlet temperature of the gas. The compressed gas temperature must be lowered to the crystallizer temperature, 298° K.

$$\begin{aligned} \text{Mass flow rate} &= .4140\ \text{Kgmol/10 min} \\ &= .04140\ \text{Kgmol/min} \end{aligned}$$

$$\begin{aligned} \Delta H &= H_2 - H_1 \\ &= 898 - 6316 \\ &= -5418\ \text{J/s} \\ &= .09930\ \text{BTU/s} \end{aligned}$$

The heat flow rate must equal the change in energy in the nitrogen stream.

$$\Delta H = U\ A\ \Delta T_{lm} \tag{47}$$

U for gases and water is in the range of 2-50 $\text{BTU/lbmol}\cdot\text{ft}^2\cdot{}^\circ\text{F}$,[30] an average of 26 $\text{BTU/lbmol}\cdot\text{ft}^2\cdot{}^\circ\text{F}$ will be used to calculate an approximate area. The coolant will be water inlet 65° F and outlet 90°F.

$$\begin{aligned} \Delta T_{lm} &= (\Delta T_i - \Delta T_o)/\ln(\Delta T_i/\Delta T_o) \\ &= (12.0-292)/\ln(12.0/292) \\ &= 87.7\ {}^\circ\text{F} \end{aligned} \tag{48}$$

$$\begin{aligned} A &= \Delta H/(U\Delta T_{lm}) \qquad (39)\\ &= (.09930)(3600)(6)/(26)(87.7)\\ &= .94\ ft^2 \end{aligned}$$

With area and pressure known, a corresponding cost can be determined form graphical data. Such data is available in Figure 14-17, Reference 30. With an area of 1.0 ft^3 and stainless steel construction, the cost is $1300.00. An adjustment factor for higher pressure is needed. Using the size adjustment factor of .44 for pressure vessels and since the change in pressure is a change in size,[30] this will be assumed to apply:

$$\begin{aligned} Cost &= 1300\ (20{,}000/600)^{.44}\\ &= \$\ 6000 \end{aligned}$$

Nitrogen Storage

A storage vessel must be used to recover the nitrogen let down from the crystallizer. The gas will be stored at 200 psi and enough gas for 5 cycles will be stored. Some loss will result from gas in solution and the volume of gas left at 200 psi.

$$\begin{aligned} Total &= .414\ Kgmol \times 5\\ &= 2.07\ Kgmol \end{aligned}$$

$$(13.3)(V) = (2.07)(87.06)(298)$$

$$\begin{aligned} V &= 3{,}805\ L\\ &= 134\ ft^3 \end{aligned}$$

This tank will be designed like the crystallizer. A radius of 36 inches and height of 60 inches will be used for a finished volume of 141 ft^3.

Shell circumferential stress:

$$\begin{aligned} t &= P \times R/(S \times E - .6P) && (40)\\ &= (200)(36)/((15000)(1) - (.6)(200))\\ &= .484 \text{ in} \end{aligned}$$

Shell longitudinal stress:

$$\begin{aligned} t &= P \times R/(S \times E - .4P) && (41)\\ &= (200)(36)/((2)(1500)(1) - (.4)(200))\\ &= .239 \text{ in} \end{aligned}$$

2 heads elliptical heads 10%

$$\begin{aligned} t &= P \times D/(2S \times E - .2P) && (33)\\ &= (200)(72)/((2)(15000)(1) - (.2)(200))\\ &= .480 \text{ in} \end{aligned}$$

The mass of the tank is necessary to complete the cost determination.

$$\begin{aligned} \text{Volume shell} &= \pi\,((R+t)^2 -{}_2R^2)\ L_2 && (35)\\ &= \pi\,((36.484)^2 - 36^2)\ (60)\\ &= 6610 \text{ in}^3 \end{aligned}$$

$$\begin{aligned} \text{Volume head} &= (4/3)\ \pi\ (a+t)(b+t)(c+t) - abc && (36)\\ &= (4/3)\ \pi_3(36.24)(18.24) - (36)(18)\\ &= 5300 \text{ in}^3 \end{aligned}$$

$$\text{Density} = .284 \text{ lb/in}^3$$

$$\begin{aligned} \text{Total volume} &= 17{,}200 \text{ in}^3\\ \text{Total mass} &= 4{,}890 \text{ lb} \end{aligned}$$

Cost from Figure 6, Reference 7, is $0.80 per pound for low alloy steel.

Cost = $ 3,900

Monsanto's Flowtran has an extensive library of unit operations to model most processes.[32] Often there is a need to develop new programs for unit processes not in the library. A program to be used in conjunction with Flowtran has been developed. This program does the work of the previous design. This is a batch process though and as such does not convert well with Flowtran. This creates problems with using the program. A listing of the Flowtran program can be found in the Appendix. Figure 14 is the output of the new Flowtran block. As seen the program reports many of the intermediate values as well as the cost of the vessel.

Distillation Column

The distillation column for comparison with the crystallizer can also be modeled by Flowtran. The overall rates will be the same but they must be converted to continuous rates. The parameters of the column were first determined by a preliminary Flowtran model which used the Underwood equation. The parameters were reflux ratio, number of trays, feed plate, bottoms pressure, condenser pressure, and distillate to bottoms ratio.Those parameters were used with a more rigorous model. The rigorous model selected the diameter. The

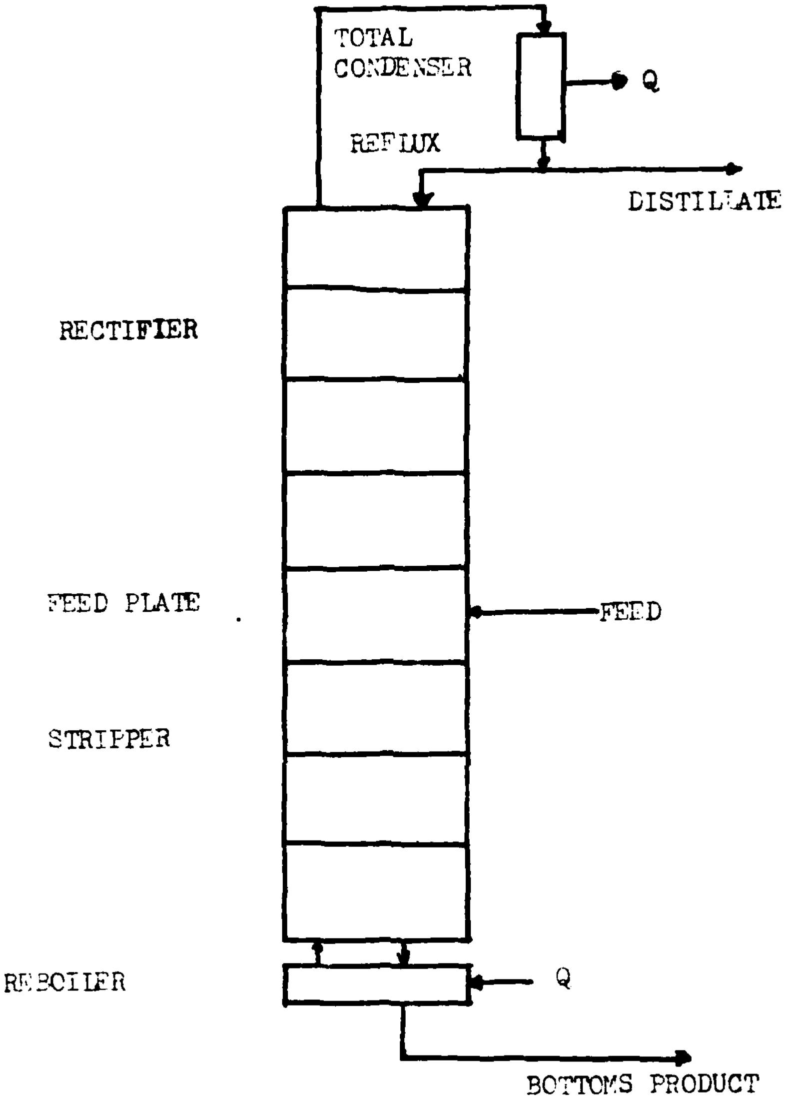

Figure 15. Diagram of distillation column

```
TITLE DISTILLATION COLUMN FOR COMPARISON
PROPS 2 1 2 2 2
RETR CH BZ
PRINT POUNDS
BLOCK DIST DISTL S1 S3 S2
PARAM DIST 1 28.9 60 45 15 13 .3982 0 0 0
BLOCK DICO CDSTL DIST
PARAM DICO 1 0 0 0
LBS S1 1 45.3 408.2
TEMP S1 70
PRESS S1 14
END CASE
END JOB
```

```
DISTILLATION COLUMN FOR COMPARISUN

PHYSICAL PROPERTY OPTIONS
   ANTOINE VAPOR PRESSURE
   REDLICH-KWONG VAPOR FUGACITY
   CORRECTED LIQUID FUGACITY
   SCATCHARD-HILDEBRAND ACTIVITY COEF
```

Figure 16. Input to Flowtran simulation

```
DISTILLATION COLUMN FOR COMPARISON

DIST   - DISTL - TOTAL CONDENSER
    FEED = S1    , BOTTOMS = S3    , OVERHEAD = S2
    REFLUX RATIO= 28.90, NO. OF PLATES  =    60., FEED PLATE= 45.
    FRAC OVHD    = 0.398, FEED FRAC VAPOR= 0.000
    CONDENSER DUTY= 0.8940E+06BTU/HR, TEMP= 176.52F, PRES=  15.00PSIA
    REBOILER  DUTY= 0.9133E+06BTU/HR, TEMP= 169.73F, PRES=  13.00PSIA


DICO  (DISTC)  COST FOR UNIT DIST
    NUMBER OF DIAMETERS           1.     REFLUX RATIO             28.900
    NUMBER OF TRAYS             60.0     TYPE OF TRAY                 3.
    MOC FACTOR FOR TRAYS        1.00     TRAY COST UPDATE FACTOR  124.0
    LOADING AT TOP              0.85     LOADING AT BOTTOM          0.85
    PLATE SPACING AT TOP         18.     PLATE SPACING AT BOTTOM     18.
    SURFACE TENSION AT TOP       20.     SURFACE TENSION AT BOTTOM  20.
    FOAMING FACTOR AT TOP       1.00     FOAMING FACTOR AT BOTTOM  1.00
    OVERALL U FOR CONDENSER    100.0     COOLANT TEMP IN           80.00
    COOLANT TEMP RISE          20.00     MINIMUM TEMP APPROACH     10.00
    COOLANT HEAT CAPACITY       1.00     COOLANT SPECIFIC GRAVITY  1.00
    CONDENSATE SUBCOOLING       0.00     PRESSURE FACTOR-CONDENSER 1.00
    TYPE OF CONDENSER            -1.     TUBE LENGTH FACTOR-COND   1.00
    MOC FACTOR FOR CONDENSER    1.00     CONDENSER UPDATE FACTOR, 124.0
    COOLANT COST-C/MGL          3.00     HEATING FLUID COST-C/MLB 56.00
    HEATING FLUID MAX TEMP    700.00     REBOILER HEAT FLUX       12000.
    MIN TEMP DIF FORFLUX        1.00     HEATING FLUID DELTA H     1000.
    TYPE OF REBOILER             -1.     MOC FACTOR FOR REBOILER   1.00
    PRESSURE FACTOR-REBOILER    1.00     TUBE LENGTH FACTOR-REBL   1.00
    REBOILER UPDATE FACTOR     124.0     SKIRT HEIGHT              10.0
    STRESS IN COLUMN SHELL    14000.     CORROSION ALLOWANCE      0.000
    EXTRA WEIGHT ITEMS         2500.     SHELL COST,$/LB           0.50

    CONDENSER-
       CONDENSER DUTY, BTU/HR =    0.89403755E+06
       LOG MEAN TEMP DIFFERENCE =   86.13 DEG F
       AREA =  103.80 SQ FT
       COOLANT FLOW RATE =    89.404 GPM
       CONDENSER COST = $     1280.00
       COOLANT COST = $/HR          0.16

    REBOILER -
       REBOILER DUTY, BTU/HR =    0.91326925E+06
       AREA =    76.11 SQ FT
       STEAM FLOW RATE =   913.269 LB/HR
       REBOILER COST = $     1030.00
       STEAM COST = $/HR          0.51

    COLUMN DIAMETERS-        COLUMN HEIGHT, FT    = 100.00
       BELOW FEED  2.0000   SHELL THICKNESS, IN  = 1.6250
       ABOVE FEED  2.0000   SHELL THICKNESS, IN  = 1.6250
       COST OF COLUMN SHELL = $    22270.00
       TRAY COST = $     3620.00

     TOTAL UTILITY COST= $/HR        0.67

     COLUMN CAPITAL COST   = $    28200.00
```

Figure 17. Flowtran output for distillation column

desired result was a column optimized between operating cost and capital cost while producing a product of equal purity to the crystallization process. The process diagram is shown in Figure 15. The Flowtran input is in Figure 16. The results of the Flowtran design are shown in Figure 17.

Crystallizer Design with Hydraulic Compression

An alternate to the high pressure design can also be proposed. Figure 18 is a diagram of the alternate design. It is still a high pressure process but, instead of an inert gas pressurizing the system the pressure is supplied hydraulically and intensified. The crystallizer, Figure 19, is a double ended piston and cylinder arrangement. On one end an incompressible fluid is pumped to supply the force on the piston. The force is equal to pressure-area of piston product. The area of the crystallizer piston is much smaller than the fluid piston allowing a large increase in pressure.

$$P_2 = P_1 \, (A_1/A_2) \qquad (42)$$

The design of these two pressure vessels and the piston will be similar to the pressure vessels presented before.

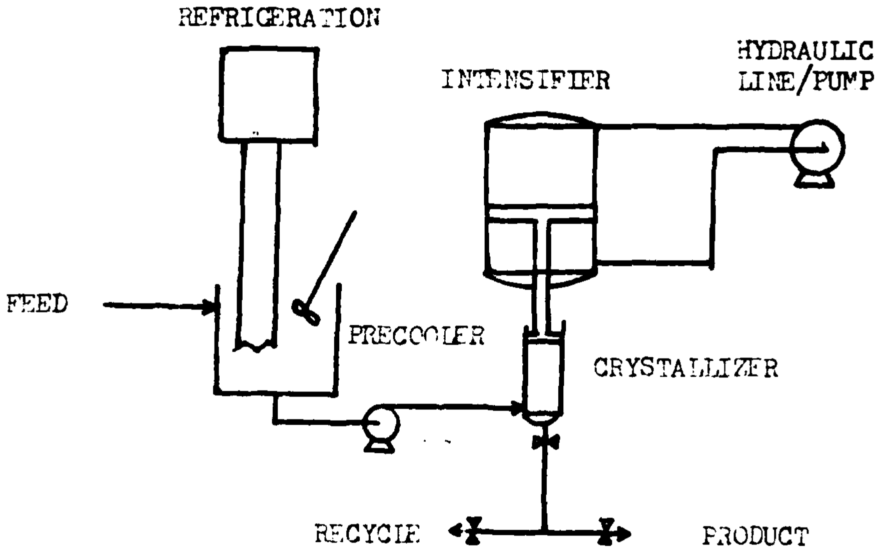

Figure 18. Diagram of hydraulically pressurized high pressurization process

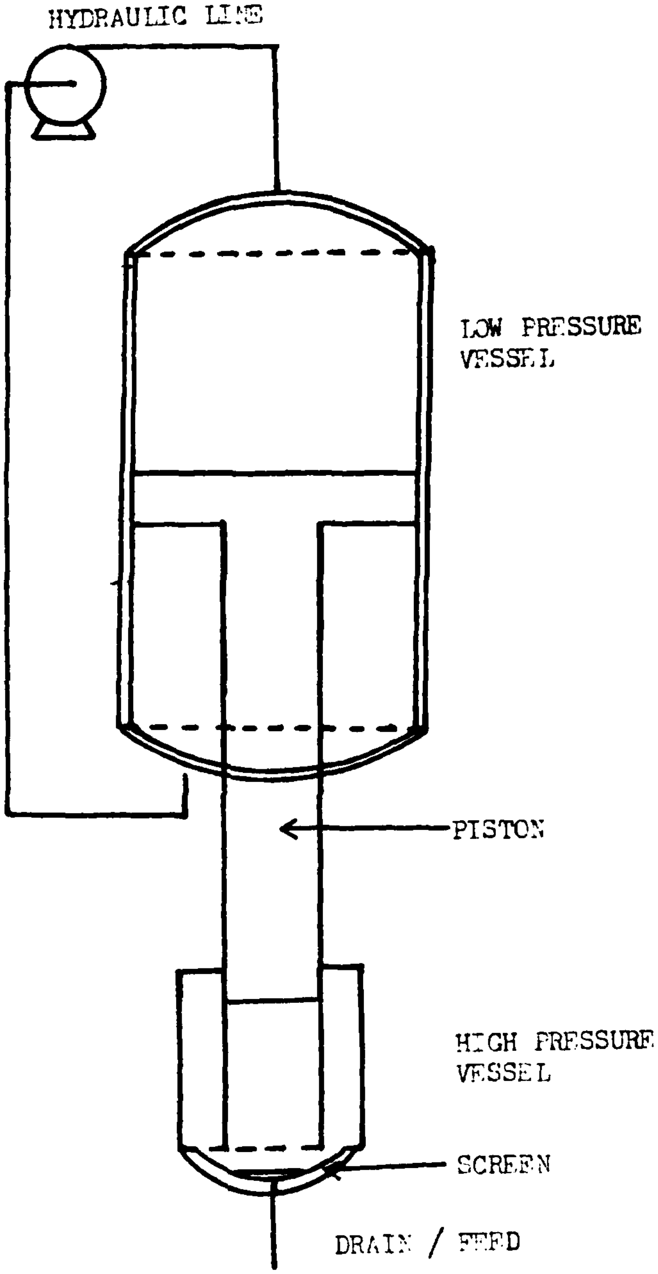

Figure 19. Diagram of crystallizer for hydraulically pressurized process.

Crystallizer Similarities

This process has several similarities to the previous crystallization process. First, the mass balances and cycle times will be the same. This will also force the crystallizer volume to be the same. The minimum work on the liquid will also be equal due to the above reasons. The minimum work will necessarily be less than the gas compression process, since there is no work on gas compression. This will also make the operation expense of this process lower than the first process. The final similarity is the precooler. The work done on the fluid and the heat of fusion liberated will be the same so the precooler size and cost will be the same.

Pressure Vessel Design

The material of construction will also be the same as the first design, 302-SS. The low pressure fluid will be 200 psi. The area difference of the two piston heads can be calculated with the vessel diameters and wall thicknesses of the shells and heads. Subscripts 1 and 2 are for the high and low pressure ends, respectively.

Area

$$20{,}000 = 200\ (A_1/A_2)$$
$$A_2 = 320\ \text{cm}^2$$
$$A_1 = 32{,}000\ \text{cm}^2$$

Radius

$$r_1 = 10.1\ \text{cm}$$
$$r_2 = 101\ \text{cm}$$
$$L_1 = 370\ \text{cm}$$

Thickness and volume of high pressure vessel are calculated as the previous high pressure vessel, p.37-40.

$$t_{SH2} = 16.2\ \text{cm}$$
$$V_{SH2} = \pi\ (26.3 - 10.1)\ 370$$
$$= 685{,}000\ \text{cm}^3$$

$$t_{H2} = 8.10\ \text{cm}$$
$$V_{H2} = (4/3)\ \pi\ [(18.2)^2(13.2)$$
$$- (10.1)^2(7.6)]$$
$$= 4500\ \text{cm}^3$$

Using the area and the volume, the crystallizer dimensions can be calculated. The volume of solid is the total volume with the liquid volume subtracted. The volume of solid will allow calculation of the piston length, since it is the maximum travel of the piston. The volume of the low pressure vessel may also be calculated from this length.

$$V_{solid} = 58.9\ \text{L}$$
$$L_{piston} = (58.9)(1000)/(320)$$
$$= 200\ \text{cm}$$

Thickness and volume of low pressure shell

$$V_{SH1} = (200)(32{,}000)$$
$$= 6400\ \text{L}$$

$t_{SH1} = 1.36$ cm

$t_{H1} = .673$ cm

$V_{SH1} = \pi\,(102.36^2 - 101^2)\,200$

$= 173{,}500 \text{ cm}^3$

$V_{H1} = (4/3)\,\pi\,((101.673)^2(51.173)$

$- (101)^2(50.5))$

$= 58{,}00 \text{ cm}^3$

Piston Volume $= (200)\,\pi\,(10.1)^2 + (10)\,\pi\,(101)^2$

Total Volume Material $= 1.306 \times 10^6 \text{ cm}^3$

Material density $= 1.77 \times 10^{-2} \text{ lb/cm}^3$

Material Cost = \$ 1.80

Total Cost = \$ 41,600

Hydraulic Pump

The pump for the low pressure fluid should be specified to pump the total amount of fluid in 2/3 of the cycle time. It can be sized from graphical data, Figure 13-42, Reference 20.

Flow rate $= (6400)/(20)(3.178)$
$= 22$ gpm @ 200 psi

The cost found is \$ 2000 for a discharge of 100 psi. This needs to be adjusted to 200 psi.

Cost $= 2000\,(200/100)^{.6}$
$=$ \$ 3100

The pump also needs a 10 hp motor which costs \$ 650 from Figure 13-56, Reference 30.

Three processes have been designed to perform the same separation. Two designs crystallize the material as means of separation. The third is a distillation process, which separates by vaporization. The summary of major equipment and operating costs for these processes is located in Table 4. The summary of operating cost is in Table 5.

Table 4
Summary of Crystallization and Distillation Processes

1. Crystallizer with gas compression

Unit	Specifications	Cost(1985 $)
Crystallizer	302-stainless steel Shell r = 25 cm l = 35.6 cm t = 40.2 cm Ellipsoidal heads r_1 = 25 cm r_2 = 25 cm r_3 = 12.5 cm t = 20.1 cm	53,200
Compressor	6.1 hp, 20,000 psi discharge,200 psi feed	29,500
Heat Exchanger	7.0 ft^3, Water coolant in at 65° F, T = 25° F	8,500
Gas Storage	Carbon Steel Shell r = 36 in l = 60 in t = .484 in Ellipsoidal Heads r = 36 in r = 36 in r = 18 in t = .240 in	6,600
Precooler	NH_3 Plant- .40 ton-day	3,200
	Mixed Tank, 40 gal	3,300
	Heat Exchanger	2,400
	Pump	815
Total Equipment Cost		$ 108,015

Table 4, Continued

2. Crystallizer with Hydraulic Compression

Unit	Specifications	Cost(1985 $)
Crystallizer	302-stainless steel	
	Hydraulyc Intensifier	
	and crystallizer vessel	
	200 psi $r = 101$ cm	
	$l = 200$ cm	
	$t = .693$ cm	
	20,000 psi	
	$r = 10.1$ cm	
	$l =$ cm	
	$t_{HEAD} = 8.1$ cm	
	$t_{SHELL} = 16.2$ cm	
	Piston $r = 101$ cm	
	$l = 10$ cm	
	$r = 10.1$ cm	
	$l = 200$ cm	105,500
	Hydraulic fluid,1600 gal	8,000
Pump	200 psi discharge	
	22 gpm	4,300
Motor	10 hp	930
Precooler	NH_3 Plant- .52 ton-day	3,200
	Mixed Tank, 40 gal	3,300
	Heat Exchanger	2,400
	Pump	815
Total Equipment Cost		$ 124,945

3. Distillation Column for Comparison

Unit	Specifications	Cost(1985 $)
Condenser	103.8 ft^2	3,500
Reboiler	76.1 ft^2	2,800
Trays	60 sieve trays	
	with downcomers	9,800
Column	100 ft high	
	18 in between trays	60,300
Total Equipment Cost		$ 76,400

Table 5
Summary of Anual Operating Costs

1. Crystallizer with gas compression

Utility	Ammount	Cost
Refrigeration	.52 ton-day/day	160
Cooling Water	30 gal/cycle	16
Electric (Compressor)	6.1 hp for 10 min/cycle	606
Nitrogen gas	46.0 SCF/cycle	4,540
Total Utilities Cost		$ 5,325

2. Crystallizer with Hydraulic Compression

Utility	Ammount	Cost
Refrigeration	.52 ton-day/day	160
Electric (Pump)	10 hp for 10 min/cycle	999
Total Utilities Cost		$ 1,159

3. Distillation Column

Utility	Ammount	Cost
Steam	914 lb/hr	10,500
Cooling Water	89.4 gpm	2,200
Total Utilities Cost		$ 12,700

V.Discussion

To compare the different processes, there must be several assumptions. First, it must be assumed that this process will be a part of a plant, which produces benzene and further processes a pure benzene product. An example could be ring closure of n-hexane producing cyclohexane. Dehydrogenation of the cyclohexane produces the benzene. Benzene can be further processed to a monomer such as phenol or styrene.

The crude benzene is first purified by a crude distillation to 90% purity. The benzene is then further purified by one of the designed processes. For this reason, land, yards, service facilities, and working capital have already been provided. The focus is economic evaluation of the purification necessary to the plant operation. Installation must be added regardless of the design selected. It will be calculated from a 30% factor of the purchased equipment cost. The percentage factors of purchased equipment cost are referred to as Lange Factors.[30] There are Lange factors to determine expenses such as instrumentation, electrical, and piping. It is assumed that these expenses would be higher for distillation than for high pressure crystallization. Also the Lange factors reported are for all chemical processing industries. The factors would not compensate for the less expensive instrumentation of the crystallization and for this reason are not included. The addition of these services would increase each process proportionally which would probably not be the best cost to compare.

The present values of the installed equipment and the present value of 10 years of operating costs are computed and the sum compared to select the most economical process.

Table 6
Installed Equipment Cost and Operating Expense

Process	Equipment	Installation	Operation		Total
			Annual	10 years	
1	108,015	32,400	5,325	40,380	180,795
2	124,945	37,500	1,159	8,790	171,300
3	76,400	22,900	12,700	96,900	196,200
4	40,900	12,300	2,400	18,200	73,400

Process 1, Crystallizer with gas pressurization
Process 2, Crystallizer with hydraulic pressurization
Process 3, Standard distillation column
Process 4, Proabd refiner[6]

The total cost for the hydraulically pressurized process is the lowest. This would probably be the process chosen. There may be other factors involved beside the cost. The plant may use many standard pumps and may not use compressors. This might influence the decision to go with the more expensive compressor design. There may also be reliablility data on compressors and piston systems that may make the use of one more attractive. The development of a pilot plant for each of the crystallizer processes could answer many of the questions about reliablility.

Table 7
Separation Costs of Crystallizer and Distillation Designs

Process	Total Installed Cost	Feed Composition	Separation Cost ($/Kg)
1	140,400	90%	.00533
2	162,500	90%	.00116
3	99,300	90%	.01270
4	205,500		
	(53,200)	98%	.00240

Process 1, Crystallizer with gas pressurization
Process 2, Crystallizer with hydraulic pressurization
Process 3, Standard distillation column
Process 4, Proabd refiner [6]

Table 7 shows the designed processes and a refrigeration type industrial process.[6] The Proabd refiner as discussed earlier operates on batch cycle and uses programmed freezing and warming to separate the feed. As shown in Table 7, the comparison of costs for separation clearly show that the high pressure processes have a sizable economic advantage over distillation and crystallization by refrigeration. The refrigeration process was reported for economic comparison for complete plants. The installed cost was estimated with Lange factors and is reported in parenthesis in the Table 7. The feed composition is also important. The Proabd refiner is the least costly but, is fed a 98% pure mixture. The effect of raising the feed impurity concentration would greatly increase the capital investment and raise the operating costs. The crystallizer would need a larger design to freeze the increased mother liquor and this would also force the operating cost higher, probably higher than the high pressure processes.

Before implementation of the high pressure crystallization process, several other questions need to be studied. The first is to gather data on specific systems of interest. A multipurpose pilot plant should be developed to study various systems and techniques of operation and control. If the gas pressurization design is selected, there is an excellent chance of a patent on the process. The hydraulic process may also be eligible for a patent. Kobe Steel does not have United States patents on the process they have designed so it may be possible to alter or improve on their design. The cycle time assumed in the crystallizer design was 30 minutes. The Kobe Steel research concluded that cycle times could be as low as 2 minutes. They report the equilibrium to be established in as low as 10 seconds. If the cycle time were reduced, the present design could be reduced in size and much less costly to construct. The construction of a pilot plant could confirm this as well as determine where various separation processes could be improved upon.

VI. Conclusions

The results of this study of high pressure crystallization can be summarized as follows:

1. The hydraulic compression crystallization process is the least expensive of the processes study. It is capable of separating the feed benzene stream for a capital cost of \$ 162,445 and operate for \$ 1,159/year. This is the lowest of the processes, Table 4.

2. The hydraulic pressurization may have some patent problems. The Kobe Steel research group has a process which is similar. They have an operating pilot plant and several patents granted and pending.

3. The gas pressurization process is close to competitiveness with the hydraulic process. It is lower in capital cost but, is higher in operating costs. The operating costs could be reduced by using a diaphragm to allow compression by filtered air instead of nitrogen. Reduction of operating costs could also be realized from a more complete recovery of the nitrogen.

4. The use of distillation for this separation is not recommended. The high cost required to operate the process would be a great deal more expensive for the expected equipment service life.

VII.Recommendations

The future of this project should proceed as follows:

1. Prior to implementation of the high pressure crystallization process data on specific systems should be gathered. A multipurpose pilot plant should be built to study these systems and to develop techniques of operation and control. If the gas pressurization design is selected, there is an excellent chance of a patent on the process. The hydraulic process may also be unique enough for a patent. Kobe Steel does not have United States patents on the process they have designed so it may be possible to alter or improve on their design. The cycle time assumed in the crystallizer design was 30 minutes. The Kobe Steel research concluded that cycle times could be as low as 2 minutes. They report the equilibrium to be established in as low as 10 seconds. If the cycle time were reduced the present design could be much less costly to construct. The construction of a pilot plant could confirm this as well as determine where various separation processes could be improved upon.

2. Other improvements could include an optimum switch from distillation to crystallization. The crystallizer will produce the high purity at low cost but, only when feed a high purity material. There could be an optimum concentration to switch separation techniques from

distillation to crystallization. In the case of this study, the optimum is probably at a feed of higher than 90% pure. With a more pure feed the crystallizer could be designed at a lower pressure and smaller cycle capacity. The pressure reduction would result from good productivity at a lower ultimate mother liquor concentration. The crystallizer capacity may also be reduced because with a more pure feed the equilibrium in the system will be achieved more quickly. The result of these factors would allow a less expensive design for the crystallizer as well as lower operating costs due to the reduction of mother liquor.

This work has possibly led to a patentable process. The application for patent has begun. If granted it would be well advised to fund a pilot plant which could answer many questions about process parameters (i.e. cycle time, feed concentrations, product purity) having influence on the overall cost. The pilot plant could be used to gather data on many systems and to determine optimal concentrations to switch from distillation to crystallization. The pilot plant could also answer some question about the reliability of the equipment used in the crystallization.

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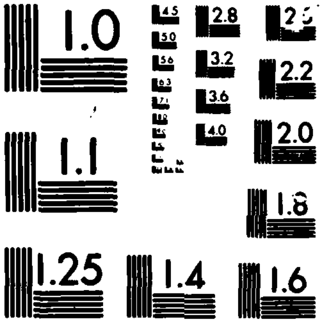
APPENDIX

```
c       This is a fortran subroutine which is
c       designed to run with Flowtran.  It is
c       block modeling a batch high pressure
c       crystallizer. The block list is 8 characters
c       long.
c       1 Block
c       2 Name
c       3 BHPC
c       4 Feed
c       5 Gas in
c       6 product
c       7 Mother liquor
c       8 Gas out
c       The parameter list has 7 pieces of data
c       to input.
c       1 Temperature
c       2 Cycle time
c       On Material of Construction
c       3 Maximun allowable pressure(atm)
c       4 Density (g/cc)
c       5 Joint eficiency
c       6 Cost/unit weight ($/lb)
c       7 Radius of vessel (in)
c       The retention vector contains:
c       1 Operating pressure
c       2 Crystallizer volume
c       specific volumes of:
c       3 Benzene liqud
c       4 Benzene solid
c       5 Cyclohexane liquid
c       6 Shell thickness
c       7 Head thickness
c       8 Shell wieght
c       9 Head weight
c       10 Crystallizer cost
c       11 Minimum work/hour
c       12 Nitrogen in solutuion
c       13 Nitrogen in space
c       14 Concentration in feed
c       15 Concentration in product
c       The units throughout the program are uniform.
c       Thicknesses or lengths are in inches.
c       Weights are in pounds.
c       Density is measured in g/cc
c       Specific volumes are in cc/g.
c       Pressure is in atm,except when some equations
c       of state are used. The units are stated and
c       converted back after calculation.
c       Time is in hours.
c       All flow rates are in pound moles.
c
        SUBROUTINE BHPC(F1,G1,P1,W1,G2,PAR,RET)
        DIMENSION F1(31),P1(31),W1(31),G1(31),G2(31),PAR(31),RET(31)
        COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
        COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
        COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
        COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
        DO 111 I=1,31
        FR(I)= F1(I)
        PR(I)= P1(I)
        AMLR(I)= W1(I)
        GI(I)= G1(I)
```

AD-A166 718 ECONOMIC COMPARISON OF A HIGH PRESSURE CRYSTALLIZATION 2/2
PROCESS WITH A DISTILLATION PROCESS(U) ARMY MILITARY
PERSONNEL CENTER ALEXANDRIA VA J E DIETZ 07 JAN 86
UNCLASSIFIED F/G 7/1 NL



MICROCOP CHART

```
         GO(I)=G2(I)
 111     CONTINUE
         NSTEP= 30
         IF(ROUT.EQ.2)GO TO 50
         CYCTM= PAR(3)
         T= PAR(1)
         R= PAR(5)
         S= PAR(7)
         E= PAR(9)
         CML = PAR(15)
         ROU=PAR(11)
         WCOST= PAR(13)
         CALL PRESS
         CALL SEP
         CALL COMPS
         CALL CRYVOL
         CALL CRYSZ
         CALL WORK
         CALL N2REQ
 50      WRITE(6,100)
         WRITE(6,101)
         WRITE(6,102) FR(20),PR(20),AMLR(20)
         WRITE(6,103) GI(20),GO(20)
         WRITE(6,104) T
         WRITE(6,105) CYCTM
         WRITE(6,106) S
         WRITE(6,107) ROU
         WRITE(6,108) E
         WRITE(6,109) WCOST
         WRITE(6,110) R
         WRITE(6,100)
         WRITE(6,101)
         WRITE(6,120) P
         WRITE(6,121) VCP0
         WRITE(6,135)
         WRITE(6,122) V0BZ,VLBZ
         WRITE(6,123) VSBZ
         WRITE(6,136)
         WRITE(6,124) V0C6,VLC6
         WRITE(6,125) TSH,WSH
         WRITE(6,126) TH,WH
         WRITE(6,127) CRCOST
         WRITE(6,128) WORKCY
         WRITE(6,150) WORKLB
         WRITE(6,137)
         WRITE(6,129) WN2SOL,WN2SPC
         WRITE(6,138)
         WRITE(6,130) C0,CS,CML
 100     FORMAT('1',15X,'HIGH PRESSURE CRYSTALLIZER')
 101     FORMAT(16X,'BLOCK - BHPC',5X,'NAME - CRYS')
 102     FORMAT(16X,'FEED = ',A4,'PRODUCT = ',A4,'MOTHER LIQUOR = ',A4)
 103     FORMAT(16X,'NITROGEN GAS IN = ',A4,'NITROGEN GAS OUT = ',A4)
 104     FORMAT(16X,'OPERATING TEMPERATURE = ',F6.2,'DEG K')
 105     FORMAT(16X,'CYCLE TIME = ',F8.4,'HOURS')
 106     FORMAT(16X,'MAXIMUM ALLOWABLE PRESSURE = ',F10.4,'ATM')
 107     FORMAT(16X,'MATERIAL DENSITY = ',F8.5,'g/cc')
 108     FORMAT(16X,'JOINT EFFIENCY = ',F8.5)
 109     FORMAT(16X,'COST PER WEIGHT = ',F8.5,'$/LB')
 110     FORMAT(16X,'RADIUS OF VESSEL = ',F8.5,'IN')
 120     FORMAT(16X,'OPERATING PRESSURE = ',F8.3,'ATM')
 121     FORMAT(16X,'CRYSTALLIZER VOLUME = ',F8.3,'L')
 122     FORMAT(16X,'LIQUID AT P0',F8.5,10X,'LIQUID AT P',F8.5)
```

```
123     FORMAT(16X,'SOLID AT P',F8.5)
124     FORMAT(16X,'LIQUID AT P0 = ',F8.5,10X,'LIQUID AT P = ',F8.5)
125     FORMAT(16X,'SHELL THICKNESS[IN]=',F8.5,'SHELL MASS[LB]=',F14.2)
126     FORMAT(16X,'HEAD THICKNESS[IN]=',F8.5,'HEAD MASS[LB]=',F14.2)
127     FORMAT(16X,'CRYSTALLIZER COST = $',F10.2)
128     FORMAT(16X,'MINIMUM WORK PER HOUR = ',F12.3,'BTU')
150     FORMAT(16X,'MINIMUM WORK PER POUND PRODUCT',F8.3)
129     FORMAT(16X,'IN SOLUTION = ',F8.2,'IN GAS PHASE = ',F8.2)
130     FORMAT(16X,'IN = ',F8.6,'PRODUCT = ',F8.6,'MOTHER LIQUOR = ',F8.6)
135     FORMAT(16X,'SPECIFIC VOLUME OF BENZENE [cc/g]')
136     FORMAT(16X,'SPECIFIC VOLUME OF N-HEXANE [cc/g]')
137     FORMAT(16X,'NITROGEN DISTRIBUTION [LB]')
138     FORMAT(16X,'CONCENTRATION OF IMPURITY (N-HEXANE)')
        END
C
C
C
C
        SUBROUTINE PRESS
C
C       This subroutine calculates the transition
C       pressure for benzene given a temperature
C       and uses as a point to define a line
C       knowing the slope of the phase diagram.
C       The line is then used to determine the
C       highest pressure needed to provide the
C       given outlet concentration.
C       FROM P.94 REF.55
C       P-Po= a[(T/To)**c-1]
C       and
C       P = -3567 Cout + I
C       Cout = outlet concentration
C       POI = intercept determined from pressure (X benxene = 1.0)
C       [P]= bars
C       [Po]= bars
C       a= 3.6 E3 bars
C       c= 2.60
C       To= normal bioling point at Po
C
C
        COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
        COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,C',CML
        COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
        COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
        A=3600
        C=2.60
        T0=278.8
        P0=1.01325
        TEMP= T/T0
        PA=1+A*((TEMP**C)-1)
        PP= PA/1.01325
        POI= -2430 - PP
        P = -2430*CML - POI
        RETURN
        END
C
C
C
C
        SUBROUTINE SEP
C
C       This subroutine determines the seperation based
```

```
c       on data from M. Moritoki, "A method of fractional
c       crystillation under high pressure," International
c       Chemical Engineering, Vol.20, No.3, p.397.
c       The Cs/Co vs. pressure curve was approximated
c       by a straight line over the 900 to 600 kg/cm2
c       range:
c               Cs/Co = .13181 - 1.1748E-4 (P).
c
c
        COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
        COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
        COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
        COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
        C0=FR(3)*84/(FR(1)*78+FR(3)*84)
        IF(P.GE.1000)GO TO 210
        CSC0= .13181 - ((1.1748E-4)*P)
 210    CSC0 = .017
        CS=CSC0*C0
        RETURN
        END
c
c
c
c
        SUBROUTINE COMPS
c
c       This subroutine assigns the flow rates of the prpduct
c       and by product streams by using mass balances.
c
c
        COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
        COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
        COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
        COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
        PROP = ((FR(1)+FR(3))*(1-CML)-FR(3))/((1-CML)-CS)
        PR(1) = (1-CS)*PROP
        PR(3) = CS*PROP
        PRINT*, 'PROP',PROP
        AMLR(1) = FR(1)-PR(1)
        AMLR(3) = FR(3)-PR(3)
        RETURN
        END
c
c
c
c
        SUBROUTINE CRYVOL
c
c       This subroutine calculates the crystillizer
c       volume given an operating pressure and the
c       physical property data on the system components.
c       The volume is calculated using the assumption that
c       cyclohexane and benzene are independent in making up the
c       volume.
c
c
        COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
        COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
        COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
        COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
        P0=1
        V0BZ= 1.138
```

```
        V0C6= 1.284
        AMSC6 = CYCTM*FR(3)*84
        AMSBZ = CYCTM*FR(1)*78
        CALL ESBZP
        CALL ESC6P
        VCP0= (AMSBZ*V0BZ+AMSC6*V0C6)*.454
        VCP = (VLBZ*AMLR(1)*78+VSBZ*PR(1)*78+VLC6*FR(3)*84)*CYCTM*.454
        RETURN
        END
c
c
c
c
        SUBROUTINE ESBZP
c
c       This subroutine calculates the volume of benzene
c       given a pressure and temperature.  It uses published data from
c       Manred Gehrig and Harro Lentz in Journal of Chemical
c       Thermodynamics, 1977, 9, p.455-450, and P.W. Bridgman
c       in proceedings of the American Academy of Arts and Sciences,
c       1949, 77, p.129-146.  Given a pressure above the transition
c       pressure the program assumes 85% solid and 15% liquid
c       because of time limitations ( equilibrium is not
c       economical to achieve ) and impurities present in the
c       solution.  The equations used are:
c
c       ( Vo-V )/V = Aln [ ( B+P )/( B+Po ) ]
c       [B]= MPa
c       [P]= MPa
c       p. 449 Gehrig and Lentz
c
c       At freezing 25 oC and 680 kg/cm2
c       DeltaV/ V= .0634 and .1596
c       p. 140 Bridgman
c
c
        COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
        COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
        COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
        COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
        V0= 1.138
        P0= .101325
        A= .1845
        B= 984.6-2.446*T
        IF (P.LE.680) GO TO 50
        PM=.101325*P
        FX= (B+PM)/(B+P0)
        DD=LOG(FX)
        VLBZ= V0/(1+A*DD)
        VSBZ= .8404*V0
        RETURN
50      PRINT*, 'ERROR "NO SOLID EXISTS"'
        RETURN
        END
c
c
c
c
        SUBROUTINE ESC6P
c
c       This subroutine calculates the volume of cyclohexane
c       given a pressure and temperature.  It uses published
```

```
c     data from Mohsen Taslimi a doctorate disertation 1969.
c     The equation  used is:
c
c     ( Vo-V)/ Vo= C log10 ( B+P )/ B
c     [P]= kp/cm2
c     [B]= kp/cm2
c     p. 41
c
c
      COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
      COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
      COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
      COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
      B= 3002 - 6.87*T
      C= .2272
      V0= 1.284
      PM= 1.03327*P
      A=(B+PM)/B
      PRINT*,A
      VLC6= V0*(1-C*LOG10(A))
      RETURN
      END
c
c
c
c
      SUBROUTINE CRYSZ
c
c     This subroutine deteermines minimum shell and
c     head thickness of the pressure vessel.  The equations
c     used are ASME standards and are taken from Max S.
c     Peters and Klaus D. Timmerhaus,  Plant
c     Design and Economics for Chemical Engineers,
c     3rd. Ed., p.570-571.
c
c     For cylindrical shell;
c
c     t = r (Z**.5 -1)
c     Z = (SE + P)/(SE - P)
c
c     For ellipsoidal heads;
c
c     t = 2 Pr/(2SE - .2P)
c
c     t = minimum wall thickness [in]
c     S = maximum allowable working stress [atm]
c     E = effiency of joints as a fraction
c     P = maximum internal pressure [psi]
c     C = corrosion allowance [in]
c
c
      COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
      COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
      COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
      COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
      PI= 3.14159
      Z=((S*E)+P)/((S*E)-P)
      TSH= R*((Z**.5)-1)
      TH=P*R*2/(2*S*E-.2*P)
      VC = VCP0-(4/3)*.01639*PI*(R**3)
      ALSH= .3937*(VC*155)/(PI*(R**2))
      PRINT*,'Z L ',Z,ALSH,VC
```

```
      VSH= ((TSH+R)**2-R**2)*PI*ALSH
      VH= (4/3)*PI*((TH+R/2)*(TH+R)**2-.5*R**3)
      WSH= VSH*ROU*16.387/454
      WH= VH*ROU*16.387/454
      WT= WSH+WH
      CRCOST= WT*WCOST
      RETURN
      END
c
c
c
c
      SUBROUTINE WORK
c
c     In this subroutine the reversable work is calculated
c     for each of the system components.  It is assumed that the
c     work is independent of composition.  The equations of
c     state used above for determining the specific volume
c     of the liquids are again used.  The reversable work,
c     the intergral of Pdv, is calculated by the Trapizoidal
c     rule over several steps, NSTEP.
c
c
      COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
      COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,C0,CS,CML
      COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
      COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
      A=.1865
      C=.2272
      NSTEP=30
      V0BZ= 1.138
      V0C6= 1.284
      DVC6= (V0C6-VLC6)/NSTEP
      BBZ= 984.6-2.446*T
      BC6= 3002 - 6.87*T
      P0=.101325
      DO 10,I=0,NSTEP
      VC6= V0C6 - I*DVC6
      CC= (V0C6-VC6)/(V0C6*C)
      PC6NEW= BC6*((10**CC)-1)*1.03327
      PC6AVE= (PC6NEW + PC6OLD)/2
      WORK2= WORK2 +  PC6AVE*DVC6
      PC6OLD = PC6NEW
10    CONTINUE
      P0=1.0
      DPR=0
      DPS=0
      DP= (P-P0)/NSTEP
      POLD=P0
      VO=V0BZ
      VSO=.9751
      DO 11, J=1,NSTEP
      PNEW= P0+ J*DP
      PAVE= (PNEW+POLD)/2
      IF(PAVE.LE.1000) GOTO 12
      CM= (PAVE+POI) /(-2430)
      PRN= .5*((FR(1)*78+FR(3)*84)*(1-CM)-FR(3)*84)/((1-CM)-CS)
      DPR= PRN-PRO
      VSN= V0BZ-((PAVE+15520)/101500)
      DVS = VSO-VSN
      IF(DVS.LE.0)DVS=0
12    AA= (BBZ+PNEW)/(BBZ+P0)
```

```
      VN= V0BZ/(1+A*LOG(AA))
      DV= -VN+VO
      WORKL= DV*PAVE*(FR(1)*78-PRN)
      WORKT= DPR*PAVE*.0962
      WORKS= PRN*PAVE*DVS
      WORK1= WORK1-WORKL+WORKT+WORKS
      VO=VN
      PRO=PRN
      VSO=VSN
      POLD=PNEW
      PRINT*,'P AVE','WORK 1','PRODUCT RATE'
      PRINT*,PAVE,WORK1,PRN
11    CONTINUE
      WORK4 = WORK1 +WORK2*84*FR(3)
      WORK4 = WORK4*.454*.0961118
      WORKCY= WORK4
      WORKLB= WORKCY/(PRN*2.2)
      RETURN
      END
C
C
C
C
C
      SUBROUTINE N2REQ
C
C     This subroutine calculates the nitrogen required
C     by the crystallizer for the benzene-n-cyclohexane system.
C     The equation of state used is the real gas law with
C     the compressibility factors found by estimating data
C     to a straight line between 200 and 1000 atm.  The data
C     was found in M. Moore, Physical Chemistry, 4th Ed.(1972),
C     p. 20. The equqtion is; Z = 1.3525E-3 P - .75100. There
C     is also the problem of the nitrogen disolving in the
C     solution. This quanity is estimated by a know mole
C     fraction of nitrogen in benzene at 25 oC and 120 atm.
C
C
      COMMON/C/ P,VCP0,VCP,V0BZ,VLBZ,VSBZ,V0C6,VLC6,TSH,WSH,POI,PRN
      COMMON/D/ TH,WH,WORKLB,CRCOST,WORKCY,WN2SOL,WN2SPC,CO,CS,CML
      COMMON/E/ T,CYCTM,S,ROU,E,WCOST,R
      COMMON/B/ FR(31),PR(31),AMLR(31),GI(31),GO(31)
      SOL = .02050
      VSPC = VCP0 - VCP
      WN2SPC = 61.6*P*VSPC/((1.3525E-3*P+.38)*82.05*T)
      DDD= FR(1)*78+FR(3)*84-PRN
      WN2SOL = (DDD/(1-SOL))*SOL
      WN2 = (WN2SOL + WN2SPC)/CYCTM
      GO(5)=WN2/28.02
      GI(5)=WN2/28.02
      RETURN
      END
```