THE DEVELOPMENT OF A SEMI-OPEN REFRIGERATION CYCLE FOR THE CRYSTALLISATION OF AQUEOUS SALTS

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THE DEVELOPMENT OF A SEMI-0PEN REFRIGERATION CYCLE FOR THE CRYSTALLISATION OF AQUEOUS SALTS.

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The development of a Semi-Open Refrigeration Cycle had been shown to be of economic value to the process of crystallisation. The experimentation took the form of several bench scale experiments to develop the designs of the individual vessels that were to constitute the final pilot plant.

In view of the safety hazards involved with a plant contacting Sulphuric Acid and Liquid Butane, a substantial Hazop and HAZAN study has been carried out.

From this data the pilot plant was constructed, with all necessary safety features. Computer monitoring and partial computer control was installed.

The pilot plant was operated as a closed loop for extended periods, to enable the production of both Iron (2) and Copper (2) Sulphates to be produced on a continuous basis.

The results showed that the crystals produced are of a small size, indicative of the instantaneous chilling of the mother liquor and are not contaminated to a significant degree with the refrigerant.

The thermal efficiency of the cycle was lower than expected at 80%, but improvements in insulation coupled with the redesign of the condenser, eliminating the necessity for a separator vessel, should increase this to the expected 90%.

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1. INTRODUCTION

1.1. Background

The topic of this research project constituted a major research investigation undertaken by British Steel plc. at its Welsh Technology Centre, Port Talbot. The project was funded jointly by British Steel and the European Economic Community, Non-Nuclear Energy Research Programme (1), and was aimed at the development of a Semi-Open Refrigeration Cycle (SORC) for crystallisation from aqueous solutions.

1.2. Application

The process can be used to crystallise any inorganic salt which can be crystallised by the chilling of the mother liquor. The immediate application of the system would be in the crystallisation of Iron (2) Sulphate from spent pickle liquor, as a direct replacement for existing acid recovery complexes at various plants throughout British Steel. However, due to its wide range of applications, it was decided that a cursory examination of other systems would be beneficial. It is desirable that the salts chosen exhibit a substantial decrease in solubility whilst ideally undergoing only a small decrease in temperature. A cursory examination of the solubility curves of some common inorganic salts (Fig. 1) (2) shows that the most common, Sodium Chloride, only exhibits a small decrease in solubility over a wide temperature range and, therefore, is not suitable for crystallisation by chilling. The most amenable salts to the chilling crystallisation processes are the Sulphates and Nitrates of Sodium, Copper (2) and to a lesser degree Iron (2). Iron (2) Sulphate actually shows an inversion of the solubility curve at ~65°C, enabling its crystallisation to occur through both chilling and evaporation processes. Sodium and Copper (2) and Iron (2) Sulphates were selected to be examined during the trials.

1.3. The Acid Recovery Process

1.3.1. The Pickling Process.

Prior to the cold rolling of steel strip at a finishing plant, it is necessary to remove the scale formed during cooling after hot rolling and thus prevent surface damage to the strip during further processing.

The normal method of scale removal is to pass the strip through a series of acid baths, this process is termed "pickling". A typical, Sulphuric Acid, Continuous Pickling Line (3) is shown in Fig. 2.

The mechanisms for the handling of steel coils can be seen at both exit and entry ends of the line.

The strip passes through 4-6m long, shallow, acid proof compartments separated by a system of weirs. Recovered Sulphuric Acid is fed into the final tank only and flows in cascade counter-current through the earlier tanks. From the first tank i.e. the entry end, this acid (spent pickle liquor) is transferred to the acid recovery plant. The solution in all tanks is maintained at a temperature of 90-95°C, normally by use of sparge steam injection or a steam/acid heat exchanger.

Typical concentrations for a 5 tank system are given in Table 1.

Following immersion in the acid, the strip passes through a rinsing and drying system. To ensure that no further degradation of the surface quality occurs prior to further rolling, the dry strip is coated with oil. This also has the effect of acting as a lubricant during cold rolling.

1.3.2. The Treatment of Waste Pickle Liquors.

One of the major management problems associated with an acid pickling plant is the disposal of the spent acids. The two chief alternatives are dumping, with or without neutralisation, and an acid recovery plant. The ultimate decision takes into consideration both environmental and economic factors.

1.3.2.1. Neutralisation.

A typical acid neutralisation plant (4) relies on the reaction between the acid and an alkali such as milk of lime ($Ca[OH]_2$). The waste liquor, containing approximately 5% sulphuric acid and 20% iron (2) sulphate is mixed with a lime slurry in a launder leading to an agitated conditioning tank. The chemical reactions involved are:

$H_2SO_4 + Ca[OH]_2 = CaSO_4 + 2H_2O$

$FeSO_4 + Ca[OH]_2 = CaSO_4 + Fe[OH]_2$

Following the completion of the reaction, the mixture is passed to a settling tank, where a flocculating agent is added to assist precipitation. The resultant sludge can be removed for disposal.

The drawbacks to this system are:

(a) high material costs.

(b) high cost of replacing the process acid.

(c) treatment is carried out on a batch basis.

(d) to reduce the acid losses the pickle line is operated at acid concentrations well below those desirable. To maintain surface quality the strip speed is reduced, losing both production and energy efficiency.

1.3.2.2. The NORDAC System.

The inversion of the solubility curve for Iron (2) Sulphate at 64.4°C makes it possible to utilise both cooling and evaporation for Iron (2) Sulphate removal from its mother liquor. The crystals formed by the evaporation process are of the mono-hydrate form.

The use of electric immersion heaters to heat the mother liquor has been described by Smallwood(5), but by far the most popular method, certainly in the UK., has been the adoption of the NORDAC (6) system (Fig. 3).

Waste pickle liquor is pumped from the pickle line to a common acid tank, where it is stored prior to being fed to either of two evaporators. As it enters the evaporators it is injected with concentrated sulphuric acid (B.O.V.) to raise the acid content to 16% w/v. The evaporators are natural gas fired units constructed of rubber lined steel. The submerged burner is rated at 6 GJ/h and is ignited by the use of a pilot burner.

Waste gases from the combustion pass, via a partially submerged steel and refractory dip-tube, into the evaporator body where they bubble through the waste pickle liquor. Evaporation of the mother liquor and the decreased solubility of the iron (2) sulphate at these elevated temperatures produces crystallisation. The contents of the evaporator are agitated by an aerator and are then air-lifted from the evaporator to the cooler/settler.

In the cooler/settler the liquor separates out into a slurry and a recovered acid stream. The slurry is fed to a centrifuge, where the mono-hydrate crystals are removed and the remaining liquor recycled to the cooler/settler. Recovered acid is removed from the top of the cooler/settler and pumped to storage.

A cost comparison between mono-hydrate production and neutralisation using milk of lime has been carried out by Alwood (7). This shows that the treatment costs of the Acid recovery system are higher than those encountered in the neutralisation process, especially when the maintenance costs are taken into consideration. However, this is more than compensated for by the improvement in both pickle line production and the quality of the pickled product.

1.3.2.3. Chilling Methods- The Lurgi System.

The design of acid recovery plants using chilling methods, and thereby producing the more commercially viable hepta-hydrate crystal, varies widely :-

(i) A batch system (8) utilising refrigerated glycol passing through heat exchanger panels inside a stirred tank, was the first to be adopted on a commercial scale. The acid is simply chilled until the iron (2) sulphate concentration reaches saturation point at the heat exchanger surface. This results in the formation of crystals on the panel surface, these have to be removed periodically in order to maintain crystalliser efficiency.

(ii) The major continuous system utilised is the Lurgi Process (9), Fig. 4. In this process, the spent pickle liquor containing 60/70 g/litre of Iron, is subjected to a vacuum treatment where the pressure above the liquor is reduced using steam ejectors to 5 Torr. The effect of this is to cause water to be lost from the system resulting in both the concentrating and chilling of the liquor to approximately 5°C. Under these conditions the hepta-hydrate crystals of Iron (2) Sulphate are precipitated. To assist in the chilling process, two pre-coolers cool the acid liquor from 85°C to 40°C by flash evaporation prior to entry into the horizontal crystalliser.

The steam from the ejectors, together with the aspirated vapours, pass to a water mixing condenser, the warmed cooling water finally being pumped to an external cooling tower.

The crystal rich slurry at 5°C, is pumped via a thickener, to a centrifuge, where the crystals are separated from the liquor as Iron (2) Sulphate hepta-hydrate.

The regenerated liquor at 5°C is fed to acid condensers where it is heated to approximately 45°C prior to being returned to the line tanks. Concentrated sulphuric acid is added to maintain the required acid concentration.

Maintenance of the system especially on the acid scrubbers and the condensers is intensive and consequently the system operates at well below its design capabilities for long periods. The result is that the recycled acid is returned to the pickle line at temperatures far lower than the design temperature with the subsequent high energy cost at the pickle line.

1.3.2.4. Alternative Methods.

One of the most recent developments in the recovery of pickle acids is in the application of an ion exchange resin (10). The performance of the acid purification unit is very dependent on the conditions of the entering acid, but in general, the recovered acid is cleaner than that from most alternative systems. However, this system has a number of drawbacks, the most significant of which is the production of a high volume of low acid level waste, which under present legislation must be neutralised prior to disposal. This means that the neutralisation / effluent plant must handle a higher volume of waste than normal and consequently disposal costs can be increased.

1.4. Approach to the Problem.

The SORC system (11) utilises direct contact heat transfer between a volatile refrigerant and the process medium. The use of direct contact heat exchange enables the attainment of high efficiencies in both evaporation and condensation regimes.

The design of the pilot plant incorporated :-

(i) direct contact heat transfer between the vaporising refrigerant and the contaminated process liquor, resulting in chilling and the subsequent crystallisation of the contaminant.

(ii) direct contact heat transfer between the condensing refrigerant and the recovered process liquor.

(iii) separation of the condensed refrigerant and process liquor into two pure components.

(iv) recovery of the liquid refrigerant in a condition suitable for re-use in (i).

A simple schematic arrangement of the process is shown in Fig. 5.

The research topic chosen was the design and development of the proposed pilot plant. To enable this to be constructed, it was necessary to evaluate the rates of evaporation, condensation and separation in order to balance the system with respect to flows, temperatures and pressures. For this reason it was necessary to investigate the performance of individual vessels prior to embarking on the design of the full system.

The crystalliser and condenser performances were evaluated by the use of test rigs which are described in **Section 6.1.** and **Section 6.4.** respectively.

The flash vessel performance was not to be investigated but was designed from thermodynamic principles.

The separator was evaluated using a transparent PVC container filled with liquid n-Butane and an aqueous solution of Copper (2) Sulphate. These experiments are discussed further in **Section 6.2.**

The data collected was used to design the pilot plant, which was constructed at the Energy Department Research Compound at British Steel, Port Talbot Works. A detailed description of the plant is contained in **Section 3**.

2. REVIEW OF RELEVANT LITERATURE .

2.1 Application of Direct Contact Heat Transfer

It should be noted that, throughout this section the units used are those of the original authors and, therefore, have not been converted to SI units.

The use of Direct - Contact heat transfer is of paramount importance in the Chemical Industry. In order to fully utilise the available heat content it is desirable that a phase change takes place during the operation. The advantages of such a system are:

1. No reduction in heat transfer coefficients due to scale or crystal formation.
2. The equipment is of relatively simple design.
3. Closer temperature approaches between the fluids can be obtained because of the high heat transfer coefficients which result from direct fluid/fluid contact.

The systems are not however without their disadvantages:

1. There is a requirement that large volumes of fluid are circulated and contacted and subsequently separated.
2. Large vessel volumes are required and consequently a high fluid inventory.

The initial work in the field has been in search of an efficient economic desalination process but new desalination processes adopt reverse osmosis as its mechanism.

Initial desalination of sea water was proposed by Wilke (12) using a hot liquid (Aroclor at 130°C) . The production rate was ~ 50 000 m^3/day of recovered water the process being dependent on the immiscibility of the two liquids.

Wiegandt (13) developed the use of the freezing process in desalination based on the fact that the ice crystals formed are free of salt and, therefore, are a source of pure water. The process is aimed at bringing about the ice/brine separation economically with high yield as well as ensuring the thermodynamic cycle responsible is so integrated into the process that minimum energy is expended. The selection of iso-Butane was made because under design conditions as the least volatile hydrocarbon considered it would not be under partial vacuum at the lowest point in the cycle.

Both of the normal alkanes (Butane and Pentane) considered can form Hydrates which have often resulted in pipeline blockages. It should be noted here that, for the experiments reported in this Thesis, n-Butane has been used. The ability of n-Butane to form a hydrate was considered during the initial design stage but due to the relatively short operating periods and the fact that the aim of the work was to develop a cycle that would be capable of operating with a number of commercially available refrigerants, it was decided that the risk was minimal. It was believed that the accessibility and cost effectiveness of commercial grade n-Butane outweighed this drawback.

Denton et al (14,15) developed 7000 and 20000 lbs/day plants at AERE Harwell using Butane as a refrigerant. The use of a continuously stirred crystalliser was considered to be ineffective since at high Butane flowrates the turbulence caused by the evaporation was far in excess of that produced by the mechanical paddle. The other major problem encountered during operation was the accumulation of Butane in the post-freezing wash column. As a consequence during testing of the SORC pilot plant samples were taken periodically from the vessels.

Other work in the area points towards the use of other refrigerants and applications but Fowles (16) uses n-Butane as the refrigerant in a process for the recovery of Durene crystals, but the recovery of the vapour produced is by compression and condensation in a separate condenser. Hendrix (17) proposes a system for the preparation of Glauber Salt using Butane as the Refrigerant, but perhaps the most relevant is the US patent of Goldberger (18) , who actually proposed the use of n-Butane to recover spent Sulphuric Acid pickle liquor, the same aim as this work. The major difference is that the n-Butane is evaporated in the spent pickle liquor to form a crystal slurry. This is separated to give crystals of Iron (2) Sulphate . The Butane vapour from the crystalliser is recovered and used as a fuel for the roasting of these crystals. The Sulphur Trioxide formed is absorbed back into the now cold recovered acid to increase its strength. In view of the large amounts of n-Butane consumed, a high cost energy source, the process, as far as is known, never reached production.

The criteria for the use of specific crystalliser designs to suit differing systems has been carried out by Schielphake (19) . A survey of available crystalliser designs has been discussed by Wohlke (20) and a simplified method of designing direct contact coolers is given by Bras (21) . However, none of these authors has mentioned the use of direct contact evaporating crystallisers or direct contact condensing coolers.

Fair (22) gives examples of designs suitable for contacting gas and liquid with the possibility of condensation. Design equations are presented for packed bed contactors, which find wide use in the chemical industry, based on mass transfer relationships.

The heat transfer coefficients given are:

$$h_g a = \left(\frac{Sc_g}{\Pr_g}\right)^{\frac{2}{3}} \frac{c_g G}{H_{g.d}}$$

$$h_l a = \left(\frac{Sc_l}{\Pr_l}\right)^{\frac{2}{3}} \frac{c_l L}{H_{l.d}}$$

The performance relies on the efficiency of the packing which was developed by Cornell (23) to give:

$$H_{g.d} = \frac{\Psi Sc_g^{0.5} D_t^{n_1}}{(L f_1 f_2 f_3)^{m_1}}$$

$$H_{l.d} = \Phi C_F (Sc_l)^{0.5}$$

where

$$f_1 = \left(\frac{\mu_l}{2.42}\right)^{0.16}$$

$$f_2 = \left(\frac{62.4}{\rho_l}\right)^{1.25}$$

$$f_3 = \left(\frac{72.8}{\sigma}\right)^{0.8}$$

These results are based on the application of film theory but penetration theory also produces liquid phase heat transfer coefficients given by Wiegandt and Harriott (24) as:

$$\frac{h_l}{k_l} = \frac{\sqrt{\left(2C_l\rho_l k_l'\right)/\pi\theta_l}}{\sqrt{2D_l/\pi\theta_l}} = \sqrt{\frac{C_l\rho_l k'_l}{D_l}}$$

The equation only holds for columns less than 600 mm diameter but under these constraints the volumetric heat transfer coefficients obtained were 50 000-150 000 Btu/h/ft^2/^{o}F.

2.2 Related studies in heat transfer from evaporating droplets

The study of vaporisation of a single droplet in an immiscible medium has been covered extensively by Lench (25) and , therefore, only a cursory review will be carried out here.

The study of evaporation was initially carried out by photographic analysis of the systems. Sideman(26) and Taitel(27) have shown from cinematic studies that evaporating drops have vapour at the top with the liquid at the bottom, again the usual assumptions are made for spherical bubbles to give the analytical solution:

$$Nu_c = \left(\frac{3\cos\beta - \cos^3\beta + 2}{\pi}\right)^{0.5} (Pe_c)^{0.5} = C(Pe_c)^{0.5}$$

where β is equivalent opening half angle of the vapour phase in a two-phase drop, the maximum heat transfer coincides with $\beta=135°$ and C=0.27.

The overall heat transfer coefficient related to the instantaneous total area of the rising two-phase drop increases sharply with evaporation up to 3-10% wt. vapour content and then decreases until evaporation is complete, indicating the decreasing effect of the internal resistance to heat transfer in the first stages of evaporation and the moderate decrease in the transfer area in the subsequent stages of the process.

For instantaneous overall heat transfer coefficients the values obtained are

200-400 Btu/h/ft^2/°F for initial diameters = 3.5 mm.
500-700 Btu/h/ft^2/°F for initial diameters = 2 mm.

The beginning of the evaporation process where internal resistance is controlling is found to take up to 50% of the total evaporation time. Pinder (28) used 3-D photography to estimate the interfacial areas of evaporating drops, later with Prakash (29) the total evaporation time was investigated. The results found were compared with the results of Sideman and Taitel (30) and Klipstein (31) and were found to agree with the latter. The overall heat transfer coefficient was found to be :

$$q_A = Cd_i^2 \Delta t$$

A number of authors have based their theories on the work of Sideman and Taitel(30) : Battya (32) used parametric studies of evaporation in a stagnant column to obtain

$$Nu = 0.64 Pe^{0.5} Ja^{-0.35}$$

based on their results.

Raina and Grover (33) used their figures in obtaining the final calculation of heat transfer for a water desalination theoretical model to give:

$$h_c = K_l \left(\frac{3U_\infty}{2\pi R \alpha_c} \right)^{0.5} (\cos\beta - (1/3)\cos^3\beta + \tfrac{2}{3})^{0.5}$$

where

$$3\cos\beta - \cos^3\beta + 2 = \frac{4(1-x)}{1+x(m-1)}$$

x =weight % of vapour in the bubble
m =ratio of liquid to vapour density in the bubble

The effect of drop diameter was considered by Calderbank and Moo-Young (34) to give:

$$Nu = 2 + 0.31(\mathrm{Ra})^{\frac{1}{3}}$$

$$Nu = 0.42 \left(\frac{\Delta\rho g D^3}{\mu_c^2 a_c} \right)^{\frac{1}{3}} \mathrm{Pr}_c^{\frac{1}{3}}$$

where the Rayleigh Number (Ra) is given as $D^3 g \Delta\rho / \mu_c a_c$

Mori(35) used the supposition that the liquid phase in each bubble forms a bottom layer supported by a flat base whilst the rest of the bubble is occupied by a heat insulating vapour phase. The heat transfer is assumed to occur at the rear of the bubble covered by a wake. The relationships given are :

$$N_u = 5.01 \times 10^{-6} Re^{\frac{7}{4}} \mathrm{Pr}^{0.5} \text{ for } Re \leq 6 \times 10^7$$

$$N_u = 1.67 \times 10^{-3} Re^{\frac{13}{12}} \mathrm{Pr}^{0.5} \text{ for } Re \leq 2.5 \times 10^4$$

2.3 Related Studies in Heat Transfer from Condensing Bubbles

Much of the work in this sphere has been carried out by Sideman et al (36-40) and Moalem et al (41-43) in Israel and continued by other researchers under their guidance. The principle has obviously been aimed at efficient desalination plants due to the country's water shortage.

Sideman and Hirsch (36) used motion picture studies for iso-Pentane in water and noted two distinct regions. Turbulent is where there was up to 80% liquid content, the bubbles deform and oscillate, heat transfer occurring by turbulent convection. The second region is where the heat transfer is controlled by the resistance of the condensed liquid and heat is transferred mainly through conduction. The effect of up to 3.5°C, on heat transfer coefficients could not be isolated, but the effect of initial bubble diameter was significant.

Raina and Wanchoo (44,45) have obtained a theoretical expression for the prediction of instantaneous heat transfer coefficients for evaporating and condensing two-phase

Raina and Wanchoo (44,45) have obtained a theoretical expression for the prediction of instantaneous heat transfer coefficients for evaporating and condensing two-phase drops and bubbles, and have used the data of other authors to validate the model. The model utilises the reports of Simpson (46) and Sambi (47) on the dispersed phase changing form whilst evaporating or condensing through a continuous fluid.

The collapsing bubble has been shown by Harkins (48) to approximate to a sphere when rising freely in a vertical path. This was based on the internal viscosity between water and a mono-layer of normal chain alcohol is 10^4 to 10^8 times larger than that of water itself. The resulting surface viscosity in effect results in a "rigid" sphere.

Moalem and Sideman (42) observed that the collapse of a single bubble can be either Heat Transfer or Liquid Inertia controlled and occasionally by both.

Condensation in a highly sub-cooled liquid is inertia controlled but bubble collapse (or growth) in a liquid with a small sub-cooling is practically independent of liquid inertia and is controlled by the rate of heat transfer across the wall of the bubble. Florschuetz and Chao (49) point out that the characteristic collapse time for a purely heat transfer controlled case is:

$$\propto (R_o^2/k)/J_a^{0.5}$$

whereas the Inertia controlled case is:

$$\propto (R_o^2/k)/C_1^{0.5}$$

where $C_1 = R_o^2(P_\infty - P_{lo})/\rho k$ and $(P_\infty - P_{lo})$ denotes the final system pressure minus the initial equilibrium pressure.

A general review of phase change direct contact heat transfer is given by Sideman (50) For the Inertia controlled case the classical Besant and Rayleigh analysis yields

$$t = 2Ro(3\rho_l/8(P_\infty - P_{i0})^{0.5} \int \frac{\beta^{3/2}}{(1-\beta^3)^{0.5}} d\beta$$

For heat transfer controlled collapse, Sideman (50) obtained :

$$R_t = 2(\tfrac{3}{\pi})^{0.5} Ja' (\alpha t)^{0.5}$$

$$\Upsilon_h = 1/3[(2/\beta) + \beta^2 - 3]$$

where $\Upsilon_h = (4/\pi)(J'_a)^2 F_0$

and $Ja' = \rho_l Cp_l (T_s - T_\infty)/\lambda\rho_v \ : \ F_0 = \alpha_1 t/R_0^2$

Where (T_s) and (T_∞) are defined in Fig. 6.

The effects of curvature and radial convection on the heat transfer bubble growth regime were analysed by Moelam and Zijl (43) to give :

$$R_t = (3/\pi)^{0.5} Ja' [1 + (1 + 2\pi/3Ja)^{0.5}]$$

for Ja ≥1, this converges to Scriven (51) and Plesset & Zwicks (52) solution for large bubbles:

$$R_t = 2(\tfrac{3}{\pi})^{0.5} Ja' (\alpha t)^{0.5}$$

For smaller bubbles where the curvature terms dominate, the solution is given by:

$$R_t = [R_0 - \frac{2Ja'\alpha t}{1+(\alpha/D_{AB})^{0.5}\gamma]^{0.5}}]^{0.5}$$

For a pure system , i.e. having no inerts and also no uncondensables this becomes:

$$R_t = [R_0^2 - 2Ja'\alpha t]^{0.5}$$

In the case of a two component, 3 phase system, as in the case of n-Butane/Water, the condensate stays within the confines of the bubble wall (51)

The largest changes in volume and area occur at the initial stages of condensation.

The turbulent region of high deformation extends until 80-90% (wt.) of the mass condenses in the bubble. Heat transfer reduces appreciably in the final laminar section as the internal resistance of the condensate to heat transfer dominates the mechanism. Despite the reference to deformation, the analyses are invariably limited to spherical bubbles.

Sideman and Isenberg (40) simplify the situation to give:

$$K_v = 0.25(\mathrm{Pr})^{-\frac{1}{3}}$$

$$\beta = \frac{R}{R_0} = [1 - (\tfrac{3}{2})(K_v/\pi)^{0.5}\Upsilon_0]^{\frac{2}{3}}$$

or

$$\Upsilon_0 = Ja' Pe^{0.5} F_0 = \tfrac{2}{3}(\pi/K_v)^{0.5}(1 - \beta^{\frac{3}{2}})$$

where

$$Ja' = \rho_l Cp_l (T_s - T_\infty)/\rho_v \lambda$$

representing the effect of the nominal temperature drop across the bubble

$$Pe = 2R_0 u/\alpha$$

representing the rise velocity temporal parameter.

$$Fo = \alpha t/R_0^2$$

representing the temporal parameter.

Overall heat transfer coefficients have been quoted by a number of authors for various systems:

Wigandt (53) reported heat transfer coefficients, for the condensation of iso-Butane in an ice column, of 3300-5000 kcal/h/cm^2 with ΔT of 1-3°C.

Bankhoff (54) reported heat transfer coefficients for steam in water of 6.5×10^4 to 15×10^5 kcal/h/cm^3 .

15×10^5 kcal/h/cm^3.

Grassman and Wyss (55) utilising only partially condensing steam bubbles gave 6.8-9.8 $\times 10^4$ kcal/h/cm^3.

The difference between the figures may be due to the greater turbulence in the Bankhoff system.

Wanchoo & Raina(45) using a boundary layer approach for fluid flow and a moderately high Reynolds Numbers obtained the relationship:

$$Nu_c = \frac{0.4886 * K_d \alpha_d^{-\frac{1}{2}} \sqrt{Pe_c}\, I[A] \sqrt{D_c}}{K_c \alpha_c^{-\frac{1}{2}} + K_d \alpha_d^{-\frac{1}{2}}}$$

Where A is a function of the physical properties and represents a measure of two-phase bubble rigidity and is given by:

$$A = \frac{4b}{\sqrt{3\pi Re_c}}$$

b =property parameter $= \dfrac{2+3\mu_d/\mu_c}{1+(\frac{\rho_d\mu_d}{\rho_c\mu_c})^{\frac{1}{2}}}$

D_c =diameter correction factor $= \left(\dfrac{-D^2+D_i^2}{2DD_f}\right)$

$I(A)$ =the definite integral defined as :

$$\int_0^{\beta_s} \frac{F(\theta)\partial\theta}{\left[\int F(\theta)\partial\theta - \left(\int F(\theta)\partial\theta\right)_{\theta=0}\right]^{\frac{1}{2}}}$$

where θ =polar angle, and:

$$F(\theta) = \sin^3\theta\left[1 - A\left(\frac{\frac{2}{3} - \cos\theta + \frac{1}{3}\cos^3\theta}{\sin 2\theta}\right)^{\frac{1}{2}}\right]$$

β_s =angle of separation (Fig 6)

β =angular distance to the condensate pool.

Kalman and Letan (56) have developed relationships from the figures of Sideman assuming a rigid mode and no condensate film. This may be assumed for some systems but it is notable that the general view is that in aqueous / hydrocarbon systems a condensate layer does exist around the bubble.

The bubble detached from its nozzle accelerates and then decelerates. Outside the accelerating bubble heat is convected across a boundary layer and a wake. On deceleration the bubble settles into its wake.

In this paper collapse is not based on bubble dynamics but is heat transfer controlled. The discriminating values between the inertia and heat transfer controlled conditions have been classified by Chao (57) for a miscible system, but have yet to be established for immiscible systems. However, Jacob Number (Ja) operation ascertains the mode of heat transfer to dominate the process.

The rate of heat transfer from the bubble to the surrounding liquid is given as:

$$\mathbf{Q} = {}_0\int^{\infty} \frac{\pi R_0 (T_s - T_\infty)\sin\theta}{\frac{1}{2k_f}\left[\frac{1}{R_v} - \frac{1}{(R_v + \delta_f)}\right] + \frac{R}{Nuk_f(R_{v} + \delta_f)^2}} d\theta$$

where

$$R_v = \left[\frac{R^3 - (\rho_v/\rho_f)}{1 - (\rho_v/\rho_f)}\right]^{\frac{1}{3}}$$

Kalman employs a drag coefficient of a spheroid to conclude that:

(i) The thermal resistance inside the bubble increases with the thickness of the accumulated condensate.

(ii) The ratio of inside to outside thermal resistance varies with the collapse rate.

The major flaws in this approach are that there is a condensate layer formed which must give rise to a thermal barrier, and the possibility of a high shear force or high velocity may result in detachment from the bubble, factors not considered in the work..

Sudhoff (58,59) carried out a series of tests on the condensation of Butane in a counter-current flow of water. A vessel, 140 mm in diameter was used and condensation took place at an elevated pressure of 2.8 bar.

He observed condensation heights varying from 160 - 600 mm, increasing with increasing Butane velocity and decreasing water flowrate.

He found that the condensation could be defined by three distinct regions:

(i) A turbulent region above the nozzle of approximately 100 mm. The variation of the control parameters had little effect on this region until the water velocity was below 1 cm/s.

(ii) The second region, where approximately 90% of the condensation takes place, varied between 180 - 400 mm above the turbulent region. These figures are quoted for a water velocity of 2 cm/s. It is, therefore, expected that as the water velocity approaches zero, this second region would increase. Figures quoted for 0.6 cm/s give a total condensation height of 560 mm. utilising a ΔT between the Butane and the water of ~7°C.

(iii) The third region above this point still exhibits a substantial change in temperature, indicating that some heat transfer is still occurring. The author states that total condensation is reached at the second region and the drop in temperature is due to some back-mixing. This is however only based on visual observations and the author recommends further work on the effect of column diameter and column internals. There is no information on the sparge ring used or the bubble size. The only variations were in gas velocity, water level and water flow, the latter being very high at a rate of 700 - 1300 kg/h. If equivalent velocities were to be achieved in the condenser vessel of the SORC pilot plant, the liquid flowrate would be approximately 3-5 tph., approaching the rate for a full scale demonstration plant.

The survey of current literature has shown that the vast majority of work has been carried out where the dispersed phase is considered to consist of a single droplet or bubble whilst the continuous phase is considered to be infinite. This approach, gives relationships applicable to laboratory scale experimentation, but has little relevance to industrial research, where the continuous phase is bounded by the constraints of the system or vessel and the dispersed phase consists of a multitude of bubbles or droplets interacting not only with each other but also the walls of the vessel. It is possible that some of the relationships produced could be modified to become applicable to either the crystalliser or condenser vessels of the proposed SORC pilot plant, but this is beyond the scope of the current research programme.

3. DESIGN OF THE PILOT PLANT

3.1. Choice of Refrigerant.

The choice of a suitable refrigerant for the system was limited by a number of constraints:-

(i) The refrigerant must be immiscible with water and aqueous solutions of a number of salts.

(ii) The refrigerant must be able to be separated from the water in a pure state.

(iii) It would be desirable if the refrigerant's boiling point was near to, but below, the desired crystallisation temperature at the Crystalliser pressure.

(iv) Due to the need for extensive development of the system, it was inevitable that substantial quantities of the refrigerant would be lost during testing. It was imperative, therefore, that the refrigerant chosen was commercially available at short notice and also be relatively inexpensive.

(v) The refrigerant must not react chemically with the solutions to be tested.

Table 2, shows the properties of several commercially available refrigerants (60,61). The constraint (iii), above, becomes of great importance in the choice of refrigerant, particularly in the development stage. The loss of control of the refrigerant flowrate could, in most cases, result in the total freezing of the evaporator and the inherent safety problems.

From the data available, it was decided to use n-Butane (62) as the refrigerant, having a boiling point of -0.5°C at 1 Bar absolute pressure. However, to increase availability and substantially decrease the costs it was decided to utilise commercial grade Butane (>90% n-Butane) which has a boiling point of ~-2°C at 1 Bar absolute pressure.

3.2. General Description of Test Facility.

The pilot plant was constructed in a custom built extension to the existing Energy Department research compound at British Steel, Port Talbot Works (Fig. 7). The extension consisted of a lean-to structure, with the external walls and roof constructed of pre-formed coated steel sheeting attached to a steel girder framework. The floor was constructed of concrete and sloped away from any adjoining walls.

Following discussions with H.M. Health and Safety Executive (63), a number of safety features were built into the facility:-

(i) A vision panel constructed of laminated safety glass was installed in the wall between the pilot plant and the control computer desk. This enabled a visual inspection of the pilot plant to be made from a non-hazardous area.

(ii) Improved ventilation of the extension was achieved by removing 1 metre of sheeting on the external wall and replacing this with a 25 mm galvanised steel mesh.

(iii) Communications between the computer operator and any personnel in the extension were maintained by the use of an intrinsically safe, voice actuated communication system.

(iv) An area adjacent to the extension was cleared and sloped away from the building. Aggregate was added to assist the evaporation of any liquid Butane that may have been spilt during trials.

(v) An area, 10 metres square, external to the compound boundary, was designated an area of restricted entry. High visibility tape was used to mark the boundary and signs warning of the possibility of LPG. leakage, "no smoking" and" no entry to unauthorised personnel" were strategically positioned. Flashing hazard warning lights were positioned at the four corners and operated during trials.

(vi) An intrinsically safe emergency stop/panic button was installed in the extension, enabling personnel in this area to override the computer and/or the computer operator in shutting down the system.

3.3. Materials of Construction.

The framework (Fig. 8), to which the pilot plant vessels were attached, was constructed on a L-shaped base and fabricated from steel channelling. The upright sections were braced using further lengths of steel channelling. The vessels themselves were positioned by the use of steel platforms connected to the uprights by Lind connectors, which enabled the positioning to be flexible. The process vessels were constructed of 250 mm diameter mild steel piping. To avoid rusting of the surfaces, which would result in the contamination of any crystals formed, the vessels were coated with " Prodorfilm " wall coating, which is also resistant to attack from both Sulphuric Acid and Butane. The gaskets for the vessels were made of "fluorocarbon", as recommended by the manufacturers. The vessels were constructed and tested in accordance with BS. 5500(64), hydraulic pressure testing being carried out at 15 Bar gauge pressure.

The pipework and fittings were constructed of 316 stainless steel, the pipework having a maximum operating pressure of 500 Bar. Connections were made using "Swagelok" stainless steel compression fittings.

The valves were constructed of stainless steel, seals being Viton, and were designated as fire series. Where there was a possibility of trapping liquid Butane between two shut-off valves, pressure venting was facilitated by the use of pre-set pressure relief valves.

Vent and purge pipework, away from the immediate vicinity of the vessels, was constructed from mild steel tubing. The vented vapours were passed to atmosphere in the taped-off area, at a height of 4m.

3.4 The Semi-Open Refrigeration Cycle (SORC) Pilot Plant

A schematic diagram of the SORC plant is shown in Figure 9. The pilot plant was designed to operate at 1/150th of the full scale plant and consisted of 4 pressure vessels ; crystalliser, condenser , separator and flash vessel.

The construction, instrumentation and control system of the plant was finalised and approved by the Health and Safety Executive.

3.4.1. Plant Operation

3.4.1.1. Crystalliser.

The purpose of the crystalliser is to chill the hot spent liquor by evaporating liquid Butane in it. The condition inside the vessel is such that hot liquor enters the top at 45°C and left the vessel at 6°C. Liquid Butane fed from the flash vessel, is pumped to the bottom through a distribution nozzle (Fig. 10) (comprising of 16 holes of 1 mm. diameter) and vaporises as it comes into contact with the hot liquor. (See **Section 6.1)**

Since the boiling point of n-Butane is -0.5°C , continuous evaporation occurs as the cooling process was only needed to 6°C. The efficiency of the system is based on the transfer of sensible heat from the hot liquor to the Butane. The vaporisation of the Butane means that the chilling effect is increased dramatically within the vessel. The use of direct contact heat transfer results in high efficiencies due to the absence of a transfer surface which would be susceptible to fouling.

As a result of the reduction in temperature, the liquor becomes saturated and results in the formation of Iron (2) Sulphate hepta-hydrate crystals. The crystal slurry is removed and passed to a centrifuge. The crystal free liquor is then pumped to the condenser. The crystalliser is designed to operate at a pressure of 0.2 bar gauge.

3.4.1.2. Condenser

This vessel is used to condense the Butane vapour to liquid by direct contact with the cold liquor. Butane vapour formed inside the crystalliser is removed at the top and passed to a compressor before being fed to the condenser. The vapour, compressed to 4.2 bar g., enters the condenser at ~50°C through a nozzle system. This comprised of a nozzle (Fig. 11), constructed of uPVC, with 360 holes of 0.35 mm diameter on a pitch of 10 mm. (See **Section 6.4**)

Cold liquor at 6°C is fed to the top and brought into counter-current contact with the warm vapour. The vapour gives up its latent heat during condensation thus increasing the temperature of the Butane / water (Pickle liquor) to ~40°C. The possibility of an emulsion forming at this point was sufficiently high to warrant the incorporation of a separator vessel into the system.

3.4.1.3. Separator.

The liquid Butane / liquor mixture is fed to the separator and allowed to stand for a period of ~20 minutes, depending on the relevant flowrates. Since the liquids are immiscible , two separate layers are formed with liquid Butane being on top, Butane is lighter with a specific gravity of 0.6 . The Butane is then removed from the top and transferred to the flash vessel. The warm liquor is taken downstream to be returned to the pickling tanks.

3.4.1.4. Flash.

The purpose of the flash vessel is to maintain the liquid Butane supply for the crystalliser. As Butane liquid enters the vessel the pressure is reduced from 4.2 to 0.2 bar gauge. The fall in pressure causes the vaporisation of some of the liquid Butane which is taken off and compressed before further use in the condenser . The remaining liquid Butane now chilled to 4°C is pumped back for evaporation in the crystalliser.

3.5. Heat and Mass Flowrates around the System

To enable the heat and mass flow conditions to be calculated, some basic assumptions have been made:-

(i) The liquid Butane feed to the crystalliser has been assumed to be 1 litre/minute at 0.2 Bar gauge pressure and 4°C.

(ii) The water supply to the crystalliser is at 40°C.

(iii) The flash and crystalliser vessels will be operated at 0.2 Bar gauge.

(iv) The condenser and separator vessels will be operated at 4.2 Bar gauge.

(v) For the initial operation of the system no crystallisation will be attempted and the medium used will be water.

(vi) Heat losses from the system by radiation and convection are not considered, assumed to be negligible at steady state conditions.

The details of the mass flowrates and temperatures for each section of the pilot plant design are contained in Figs 12-16.

3.6. Instrumentation

The major considerations in the selection of instrumentation were :-

(i) Compatibility with the process materials.

(ii) Ability to be interfaced with the computer.

(iii) Intrinsically safe operation

(iv) In the case of level gauges, a visual indication would be desirable.

In view of these constraints the following instrumentation was installed.

3.6.1. Level Measurement

Having considered the use of ultrasonic devices and individual level switches, it was decided to install float gauges (Fig. 17).

The units operate in a stand-pipe, of 50 mm diameter, connected to the vessel at two points, 850 mm apart. The unit is constructed in 316 stainless steel and the float can be used to indicate the top of the liquid Butane, the top of the water or the presence of a Butane/water interface. Visual indication is by means of a series of flaps which are activated by a bar magnet fixed in to the float. The remote indication comprises a transmitter and control unit. The transmitter is mounted on the outside of the stand-pipe and opposite to the visual indicator rail. Level changes cause the float magnet to operate the contacts of a reed switch/resistor chain, which is wired up as a voltage divider, to vary a tapped off electrical signal which is transmitted to the control unit. This signal is proportional to the level of liquid in the stand-pipe and provides a quasi-analogue read-out with a resolution of 10 mm.

The choice of level gauge for the separator was complicated by the desire to know not only the level of water in the unit i.e. the level of the Butane/water interface, but also the level of the top of the Butane. This was overcome by using a float that would sink through the Butane layer to float at the interface with water. The top of the Butane is measured by the installation of a stainless steel level switch, capable of being operated by a fluid of specific gravity < 0.6, in the top flange of the separator vessel.

The flash and condenser level gauges have been fitted with Butane floats ($SG = 0.6$) and the evaporator with a water float ($SG = 1$).

3.6.2. Temperature Measurement

The range of temperatures to be measured, 4-50°C, limits the choice of measuring device greatly. The most suitable device was considered to be a platinum resistance device. These have been installed strategically throughout the plant. The majority of devices have been positioned in and around the condenser vessel, so that the temperature profile along its length can be measured.

3.6.3. Flow Measurement

The measurement of water flows to and from the pilot plant does not constitute any difficulty. Turbine meters have been used, the pressure drop through these units being easily overcome by the system. A simple tachometer circuit has been constructed to convert the pulse signal into an analog signal for monitoring purposes.

Flow measurement in the hazardous area, in particular that of Butane has proved difficult. It was believed that the use of diaphragm pumps, calibrated for various air supply and back-pressures, and the development of control algorithms would enable the flow of Butane to be determined, as discussed later **(Section 5.4.2)**. The operation and control of these pumps proved difficult under the changing operating conditions.

The measurement and control of the water flow between the evaporator and condenser vessels was to be carried out in the same manner.

3.6.4. Pressure Measurement

Pressure measurement is installed in all four vessels using intrinsically safe pressure transmitters. The resulting 4-20 mA signal is conditioned and interfaced with the control computer via the Analog to Digital Converter (ADC) and Zener Safety Barrier Diodes.

The pressures to the three air operated diaphragm pumps are measured using pressure transducers. Since these are positioned in the non-hazardous area, there is no necessity for intrinsically safe units or the use of Zener safety barriers.

3.7. Control of the System

It was planned that the control of the various parameters would be achieved, during the trials, by a balance of manual control of shut-off and vent valves and by the alteration of pressures to the diaphragm pumps through the use of the computer and DAC system.

Control of the liquid Butane flow between the separator and flash vessels was to be achieved by the operation of two air actuated solenoid valves, positioned in the two pipelines from the separator vessel, from the computer keyboard. A later refinement to this system was to use the signal from the separator vessel level switch to operate one of the solenoid valves, leaving the option open for the operator to, via the computer keyboard, control the second valve.

The pressure of vapour Butane from the compressor could be controlled, manually, by the adjustment of a pressure relief valve positioned in the pipeline between the compressor and the condenser vessel.

3.8. Monitoring of the System.

The computer control and monitoring program is capable of monitoring the system parameters and displaying their values in a pre-defined format on the VDU, at intervals determined by the operator. The time interval chosen between each scan was normally 15-30 seconds during operation or 30 minutes during stand-by. The values for each scan were dumped to a data file to enable interpretation and statistical analysis of results to be undertaken at a later date.

The details of the control program are contained in **Section 5.3.**

4. SAFETY.

4.1. Hazard Identification and Analysis.

A number of methods, outlined below, were used to identify the potential hazards in the S.O.R.C. pilot plant(65,66).

HAZOP- A hazard and operability study is a procedure for the systematic, critical examination of the operability of a process. When applied to a process design or an operating plant it indicates potential hazards.

A formal operability study is the critical examination of the design, vessel by vessel, line by line. Guide words are used to help generate thought about operating conditions that can cause hazardous situations (Appendix 1). Line numbers quoted during the HAZOP refer to those indicated in Figure 5.

HAZAN- Hazard analysis is a technique for the quantitative assessment of a hazard after it has been identified by an operability study or similar technique. The sequence of events that lead to a hazardous incident is shown in a fault or logic tree so that an assessment of the likelihood of a failure or hazard can be made (Appendix 2).

DOW FIRE and EXPLOSION INDICES - This safety and loss guide, developed by the Dow Chemical Company, gives a method for evaluating the potential hazards of a process and assessing the safety and loss prevention measures required. A numerical index is calculated, based on the nature of the process and the properties of the materials in that process. The larger the value of the index, the more hazardous is the process. It may be calculated at an early stage in the process design and will indicate whether alterations or a less hazardous process should be considered. It can be a guide to the selection and design of the preventative and protective equipment needed for safe plant operation (Appendix 3).

4.2. Intrinsic and Extrinsic Safety.

Processes can be divided into those that are intrinsically safe, and those for which safety has to be engineered in, i.e. extrinsically safe.

An intrinsically safe process is one in which safe operation is inherent to the nature of the process; a process which causes negligible or no danger under all foreseeable circumstances and deviations from the design operating conditions.

The term "engineered safety " covers the design of control systems, alarms, pressure relief devices, automatic shut-down systems and fire fighting systems to contain any fire, explosion or potential hazard.

Most chemical processes are inherently unsafe, and as such the safe operation of such processes depends on the design and provision of engineered safety devices and good operating practices.

4.3. Proposed Procedures.

4.3.1. General Safety.

Any experimentation undertaken within British Steel is subject to rigid working procedures. These are outlined below. However, in the case of the operation of the Semi-Open Refrigeration Cycle there is a hazard not normally associated with steel research i.e. the use of a high vapour density hydrocarbon of low boiling point. The pilot plant contains ~80 kg. of n-Butane during trial periods which constitutes a potential hazard not only for the purpose built building but also for areas adjoining the test facility. For this reason the testing, normally of combustion systems and coke making, in the remainder of the compound was postponed during tests. Also the adjoining area was undergoing some demolition work at the time and it was imperative that the workforce was informed of the testing being undertaken and of the importance of the audio alarms used.

At all times during operation there must be at least two members of the Energy Research Department's staff present. During startup/shutdown one operator was at the control computer, behind a laminated window, with the other adjacent to the experimental rig. The operator at the computer terminal remained in contact with the other by a voice actuated communication system and by line of sight.

In the event of minor incidents, treatment was obtainable at the medical block.

Figure 18 is a site plan of Port Talbot works and indicates the Research block, Medical block and the Research Compound.

All personnel were familiar with the normal laboratory safety procedures (67).

In the event of any genuine emergency, fire or accident in the test area, the building should be evacuated as soon as possible, pressing a panic button on the way out. This would ensure that the system had been shut-down. Ambulance or Fire service may be called from the telephone in the office, Portacabin or the Cokemaking section of the compound.

Outside of the compound, the nearest point manned 24 hours a day is the control room of "C" power station.

If an operator should collapse whilst a Butane alarm is sounding and the system had not entered a controlled shut-down, a "panic" button should be pressed, the two escape sets from the box in the computer room should be taken, one set put on, with the other set put on the collapsed person. If possible the collapsed person should be removed to an uncontaminated area, bearing in mind that the escape sets only have a 15 minute air supply. The emergency services should then be called as soon as possible.

If a Butane alarm did not sound, ones own Butane monitor should be checked , the body approached and if there was still no Butane alarm then the situation should be treated as a collapse unrelated to gas, and the medical centre contacted before attempting to move the body.

Figure 7 is a plan of the compound and shows the general arrangement of the apparatus, the location of exits, fire extinguishers, telephones, shut-off valves and "panic " buttons.

Carbon Dioxide, foam and dry powder fire extinguishers were situated by the main door, together with a portable emergency shower.

The pilot plant building should not be entered until an operator, wearing a personal monitor, confirmed that the Butane detecting sensors were in working order and had not been activated. Personnel were not allowed to enter the test site unless they were wearing a personal Butane gas detection sensor, fitted with a suitable, audible alarm. Personnel not associated with the project were forbidden entry unless accompanied by a project member wearing a Butane gas sensor. A sign to this effect was located by the main door.

4.3.2. Basic Design Safety Features.

As recommended by the Health and Safety Executive (68) the following safety features were implemented in the design of the apparatus and surroundings.

The number of Butane cylinders stored in the vicinity were kept to a minimum, and the storage facility was in a secure, open-air compound.

The ventilation in the S.O.R.C. building was improved by removing the lower section of the cladding on the external walls and replacing it with wire mesh, for security purposes.

A slope away from the building was provided to allow any Butane spillage to flow away from the work area. The surface away from the building was covered with aggregate to promote the evaporation of any Butane that may have been spilled.

Notices were put up, to the effect that LPG was present and that there was a requirement to avoid ignition sources.

Blast walls were constructed between the rig and the computer control terminal and other work areas.

All pressure vessels were constructed to B.S. 5500 and all pressure relief valves were designed so that they discharged to a safe area if activated.

Water and nitrogen was used as purging media at start-up and shut-down and a check was to be made on any build up of oxygen, and hence an explosive mixture, in the system. The likelihood of this, however, was low, as predicted from the HAZOP and HAZAN studies.

4.3.3. Protective Clothing.

There were four, apparent, possible hazards to personnel working in the vicinity of the pilot plant rig; splash of sulphuric acid, splash of liquid Butane, flame/flash due to ignition of gaseous Butane and asphyxiation due to Butane in high concentrations.

The sulphuric acid (20% concentration) was unlikely to cause skin damage, although it could have severely irritated broken skin, but it would have caused serious eye damage. Therefore, the wearing of safety goggles was mandatory in the pilot plant building. A high pressure, safety shower was placed as close as possible to the rig so that any accidental spillage or leak could have been washed off immediately. The site chosen for this facility also needed to be in a safe area and along the escape route from the building. It was decided that the best position would be at the exit of the building, with shower activation being by the pulling of a single lever.

Liquid Butane would have a cryogenic effect, so contact with the skin was to be avoided by covering as much of the body with suitable protection.

Flame or flash protection again required full body coverage. Probanised cotton protective overalls, full face visors, ankle boots, gloves and safety helmets were worn at all times by all personnel involved in the operation of the pilot plant.

n-Butane is not considered to be toxic but at high concentrations it acts as an asphyxiant, and also has an anaesthetic effect. Two , 15 minute, compressed air escape sets were placed in the computer room for use in the unlikely event of a large leak occurring.

A formal Safe Operating Practice document was agreed with British Steel safety representatives and H.M. Health and Safety Executive prior to any testing taking place.

4.3.4. Operational Procedures.

The operating procedures for the pilot plant can be sub-divided into several individual systems, as follows.

All procedures were to be carried out with at least two "responsible" members of the Energy department in attendance, with one member remaining in the "safe" area at all times.

4.3.4.1. Purging and Filling.

All purging of the system was carried out in accordance with the L.P.G.I.T.A. Code of Practice (69). The purging medium used was water and the following procedures applied:

4.3.4.1.1. Crystalliser.

Both purge valves were opened and water introduced to the base until it flowed from the upper purge valve (Fig. 19). Both purge valves were then closed. Vapour Butane was then introduced at the bottom purge valve and water expelled from the drain. This continued until the water level was approximately half the height of the unit. All valves were then closed and the Butane supply disconnected.

4.3.4.1.2. Flash.

As with the crystalliser the flash vessel (Fig. 20) was filled with water and this was gradually replaced with Butane vapour. Liquid Butane was then added until the vessel was approximately three-quarters full.

4.3.4.1.3. Condenser.

This vessel (Fig. 21) was also purged with water but left full for the initiation of the start-up procedure.

4.3.4.1.4. Separator.

As with the condenser this vessel was purged and then filled with water in preparation for the start-up procedure.

4.3.4.1.5. Pipe-work.

The pipe-work was purged using the compressor (Fig. 22) to empty the flash vessel, passing the air/vapour through the pipe-work, compressor, condenser and safely out to atmosphere.

4.3.4.2. Start-up.

The computer and Butane sensor system were initialised and operative before any work was carried out. Limits were set for temperature, pressure, flow and level measurements.

Following purging and filling, the manual and air actuated process valves were opened and the Butane pump fed liquid Butane from the flash vessel to the crystalliser. This continued until the vessel pressure reached approximately 0.3 Bar, when the compressor was started and Butane vapour was introduced to the condenser. This continued until the pressure in both the separator and the condenser was approximately 4.0 Bar. This led to the solenoid valves on the flash vessel being activated in order to maintain level and pressure control of the separator. The manual valve on the water/acid exit from the separator was opened to maintain a steady flow through and level in the unit.

4.3.4.3. Normal Running.

Apart from the constraints put on the system by the safety procedures, operation was able to continue with the aim of reaching steady state conditions as soon as possible.

4.3.4.4. Normal Shut-down.

The shut-down procedure, under normal circumstances, was designed to ensure that the vast majority of the Butane inventory was held in the high pressure system, i.e. the separator and condenser vessels.

The solenoid valves were shut-off to stop liquid Butane entering the flash vessel. Then the Butane pump was shut-off as soon as the Butane level in the flash vessel was minimised.

The level of Butane in the separator vessel was allowed to increase with the subsequent loss of water from the system.

When sufficient Butane had been removed from the low pressure vessels, the pressure fell and the compressor was shut-down. The air actuated valves (Fig. 23) were then closed thus sealing the Butane into the high pressure system.

Manual valves throughout the system were then closed. The crystalliser and flash vessels were then purged with water and left full of water.

4.3.4.5. Emergency Shut-down.

The emergency fail-safe shut-down procedure was able to be initiated in three ways, as follows:

(i) The Butane sensors were alarmed at 20% and 40% of the lower explosion limit of Butane. The lower level gave an audible warning, whilst the upper level initiated the automatic safe shut-down procedures.

(ii) The operator was able to initiate a parallel shut-down mechanism, to that by the computer, by depressing a "panic" button in the S.O.R.C. room, thus shutting down the compressor; which automatically shut down the plant. Therefore, the system did not rely solely on the computer for fail-safe shutdown in the event of an emergency.

(iii) The pressure, level and flow measurements had an upper and lower safe limit imposed on them. This would "flag up" a message to the operator on the computer and requested the operator to give a view on the safety hazard. Affirmative gave the go ahead to continue, while negative initiated the automatic fail-safe shutdown procedure.

The effect of the above was to shut down all pumps, shut down the compressor and close all air actuated valves, in a predetermined safe sequence, thus sealing the high pressure system.

The Butane trapped in the crystalliser and flash vessels was allowed to vent slowly to atmosphere, via the pressure relief valves.

4.3.4.6. Emptying and Purging.

Emptying of the system would only be likely to occur when modifications to the vessel internals or pipework are necessary.

The aim would, under these circumstances, be to transfer the liquid Butane to the flash vessel, the vapour thus formed being vented to the atmosphere. The liquid Butane was to be evaporated in the crystalliser by direct contact with warm water, the water being passed to drain. The resultant vapour would be diverted from the compressor line into the vent line and to atmosphere. The control of the Butane pump would ensure that the vent rate was controlled to acceptable levels.

Each unit would then be purged with water as described earlier.

4.4. Discussion.

4.4.1. The Hazop Study.

With the aid of the HAZOP study (Appendix 1), and previous experience, every effort has been made to anticipate possible hazards and to modify the software and hardware so that in the unlikely event of an emergency, the rig would "fail-safe" without human intervention. Also, at any time the rig can be shutdown safely by the operators via the "panic" button system.

4.4.1.1. Level Gauge Failure.

The failure of a level gauge could result in a loss of control of the S.O.R.C. However, with such a situation in mind, they were designed to fail-safe. In the event of the float becoming damaged, and sinking, it would drop below the level of the Butane; the Butane having a lower density than the aqueous acid solution. No Butane could then enter any pipeline that was designated for acid solution, and no downstream problems could occur.

A maximum/minimum acceptable level was set, so that automatic fail-safe shut-down would occur if these limits were exceeded.

A level gauge however, may stick, giving the incorrect level reading to the control computer. Due to the extensive safety back-up any variation in one of the control parameters, i.e. temperature, pressure and level in each of the other units, would result in fail-safe shut-down (see HAZOP study, Appendix 1). There was a need, therefore, for the pilot plant operator to be aware of this possible occurrence and to be prepared.

4.4.1.2. Flow, Pressure, Temperature Sensor Failure/Error

Any failure or error of the control sensors/actuators, would result in abnormal signals returning to the control computer. Maximum / minimum tolerances for the various parameters were built into the control program, so that a fail-safe shutdown would be initiated if they were exceeded.

4.4.1.3. Compressor/Pump Failure.

Failure of a supply pump or the Butane compressor could result in either an increase or decrease in pressure that would lead to a build up or leak of explosive material.

If a pump or the compressor failed completely, it would have the same effect as a line blockage, i.e. the levels in units both up and downstream would be affected, resulting in control from the level gauges and possible fail-safe shutdown.

The only common mode failure of all pumps would be caused by a compressed air supply fault, which would result in all pumps shutting down. The result would be a drastic change in conditions throughout the system, these variations in level and pressure would initiate the safe shut-down procedures.

To prevent the compressor being damaged by acid entrained in the Butane vapour stream, a mist removal unit was placed in the line.

The compressor and pumps have been designed so that they would act as non-return valves to prevent any reversed flow occurring in the system.

Any increase in the line pressure beyond acceptable limits, before or after a pump or the compressor, would result in venting of the excess pressure to atmosphere via the pressure relief valves, shown on either side of the air actuated transfer pump. (Fig. 24).

4.4.1.4. Pipe/Vessel Fracture.

Any such failure would result in Butane spillage, which would produce an automatic fail-safe shutdown instigated by abnormal signals returning to the control computer and/or the Butane sensors in the vicinity of the pilot plant. In order to reduce the chance of this occurring high working pressure (500 Bar) fittings have been used. The vessels themselves have been hydraulic tested to 10 Bar, with the pressure relief valves set at 6 Bar.

4.4.1.5. Loss of Power and/or Computer Control.

Automatic fail-safe shutdown has been built into the system so that a power cut or computer failure would not be the cause of a hazardous incident. The control valves would shut if no signal was received from the control computer. Manual fail-safe shut-down would always be possible via the a "panic" button system, similar to those used in previous pilot plant projects (70,71).

4.4.1.6. Oxygen Build Up.

An explosive mixture could be formed within the S.O.R.C. due to a build up of dissolved oxygen in the Butane/aqueous acid mixture or by a negative pressure occurring in one of the units, drawing air into the system.

The maximum dissolved oxygen content is low, with a maximum of 9 mg/litre at atmospheric pressure able to dissolve in water. A positive pressure would be maintained in all units in order to reduce the possibility of any leak into the system.

4.4.1.7. Butane Sensor Failure.

In order to pick up any leak of Butane, Butane sensors have been placed around the pilot plant. An audible warning would be initiated at 20% of the Lower Explosion Limit while the sensors would initiate a fail-safe shut-down if the Butane level exceeded 40% of the Lower Explosion Limit. In the event of their failure, the alarm would sound and the system shut down, as for a leak of Butane. The operators would have to ascertain, with a personal Butane monitor whether it was a genuine leak or a sensor failure.

4.4.1.8. Ignition Source.

The pilot plant has been set up so that it would be intrinsically safe, i.e. the equipment used would not in itself be capable of producing an ignition source and hence a potential hazard (see Section 5). Zener barriers (Fig. 25) have been placed in the signal cables to and from the control computer to prevent any variation or abnormality in the electrical supply that might have provided an ignition source for any build up of explosive material.

4.4.2. Hazard Analysis.

The hazard analysis (HAZAN - Appendix 2), Fig. 26, shows that the probability of an incident occurring, which would result in catastrophic failure, is very low at 0.02625 i.e. an incident occurring once every 38 years. This is probably not accurate, due to the estimates used for the probabilities of failure of both hardware and software. However, it does show that the likelihood of an incident occurring is very low and more than acceptable for a pilot plant of short operational life.

4.4.3. Dow Fire and Explosion Index.

The Dow Fire and Explosion Index (Appendix 3), Figs. 27-31, carried out for each major unit showed that the S.O.R.C. did include several hazards. The separator posed less of a hazard than the other units, its index being in the light range, because there was no vapour Butane involved. The other three units have indices in the heavy and extreme ranges mainly due to the presence of Butane vapour.

4.5. Conclusions.

(i) The HAZOP study and Dow Fire and Explosion Index indicated that the number of potential hazards involved with the S.O.R.C was high, but that sufficient safety measures and safe operating practices could be undertaken to eliminate or reduce those hazards.

(ii) Operation of the pilot plant using level gauge control was found to be an integral part of the safety system; which justified the high capital expenditure on these items.

(iii) The other extensive safety measures; including the Butane sensors/alarms, Zener barriers, pressure relief valves, and high working pressure fittings; have also been justified, in the light of the hazards identified.

(iv) The HAZAN has shown that due to the extensive safety back-up systems; installed for the safe control and operation of the pilot plant in order to prevent a potentially dangerous leak of explosive material and/or an ignition source occurring; the likelihood of an incident occurring was low, at once in 38 years. Although this would not be considered a suitable situation for a production plant, it was , in agreement with the British Steel Safety Officers and the Health and Safety Executive, considered suitable for a pilot plant of very limited operational life.

5. CONTROL AND MONITORING EQUIPMENT.

5.1. Computer.

It was decided at an early stage that the pilot plant was to be computer monitored and, to some degree, the process was to be computer controlled.

The choice of computer was restricted due to financial constraints and also the standardisation of computers within British Steel. The computer chosen was an IBM clone, a Mertec 286, supplied by a local distributor.

The specification of the computer system was:

(i) a 1 Mbyte RAM.
(ii) a 20 MByte hard disk.
(iii) an EGA colour monitor.
(iv) a 3.5" high density floppy disk drive.
(v) a 5.25" high density floppy disk drive.
(vi) 2 serial and 2 parallel communication ports.

The interface units chosen were 2 "Thinklab" units, and communication with the computer was achieved by utilising RS232 connections to the COM1 and COM2 ports. It was decided to use one "Thinklab" purely for input data from the pilot plant, the second was to be used for outputs from the computer to the control units.

The "Thinklab" on the COM1 port consisted of:

(i) 1 card of 16 channels configured for Type K thermocouples.

(ii) 1 card of 16 channels configured for Platinum Resistance Thermometers.

(iii) 1 card of 16 channels configured for Platinum Resistance Thermometers through Zener diode safety barriers.

(iv) 4 cards of 8 channels configured for 0-20 mV signals from instruments.

(v) 1 card consisting of a 12 bit ADC integrator.

It should be noted that 8 cards is the maximum capacity of the "Thinklab" and not all cards were fully utilised.

The "Thinklab" on the COM2 port consisted of:-

4 cards of 4 channels; 12 bit DAC , 0-10 V.

2 cards of 8 channels; 110 V, 1 amp single pole relays.

Again not all channels were used, and there remained the option of adding two further cards to the two vacant slots in the "Thinklab".

5.2 Software

A number of commercially available software packages were used during the project:-

5.2.1 GW Basic

This was used for the main pilot plant control program and also for data logging. The choice of this language for this application was based on experience gained in earlier work.

Benefits of the system were :

(i) It was easy to modify any program or sub-routine.

(ii) During normal operation it was possible to break into the program loops, to make adjustments, and then continue the program without the necessity of reloading or re-compiling the program.

(iii) The package had been used for previous work and this made it possible to re-use existing sub-routines especially those for the " Thinklab ".

(iv) The use of "interpreted basic " is fast enough for the task in hand. In fact there is a built in time delay to the program which results in the computer spending half its time in a " wait " loop. This was also built into the system to ensure that there would be minimal instability in the system and reactions would not occur too quickly on the basis of small or short term fluctuations in the measured parameters.

Compiled "Basics" such as "Turbo-basic" and "Quick-basic" were available but offered no advantages in this particular application.

5.2.2 AMIPRO

This package was used for word-processing and the preparation of this Thesis.

5.2.3 LOTUS 123 v4

These were used for the preparation of diagrams and overhead slides for various presentations.

5.2.4 Other Packages.

WORDSTAR, TURBO-BASIC and HARVARD GRAPHICS were used during the project.

5.3 The Control Program

The control and monitoring program is shown in the logic diagram (Fig. 32).

At the start of a run the computer enters an initialisation sub-routine , which dimensions the arrays and sets the constants used in the program (sub-routine 15000). The two "Thinklabs" are configured to receive and transmit data (sub-routine 14000) and it sets the initial conditions such as temperature, pressure and time (sub-routine 2000).

Following initialisation, the ADC cards (Analog to Digital Converter) are scanned (sub-routine 6000) and the units converted to engineering units for display (sub-routine 5000).

The conditions are checked and control initiated if necessary (sub-routine 4000). From these results, a decision is made as to whether the plant conditions are safe, a comparison being made with the safety limits installed during initialisation. If conditions are considered to be unsafe, the system automatically initiates a safe shut down routine (sub-routine 3000), and the pilot plant is isolated.

If conditions are found to be safe to proceed, then flows are calculated and corrections applied if necessary (sub-routine 9000). Control signals are sent to the pilot plant via the DAC cards (Digital to Analog Converter) (sub-routine 7000) and to the relays (sub-routine 8000).

The VDU screen display (Fig. 33) is updated to show the existing conditions and the data printed to a log file (sub-routine 10000) on the computer hard disk. This data file, usually in excess of 200 Kbytes, was transferred to a floppy disk for further analysis on other computers, at the completion of a run.

At this point the computer enters a wait mode, where a time delay, normally 10 seconds but variable by the operator, is installed (sub-routine 13000). This ensures that:

(i) the screen display is not being constantly altered.

(ii) the control sub-routines are not reacting to instantaneous changes in the plant variables.

(iii) an opportunity is available for the operator to break into the program at a point where no control sub-routines are in operation.

The control loop is closed by the computer returning, after the time delay, to the scanning of the ADC subroutine (sub-routine 6000).

5.4 Calibration of Pilot Plant Instrumentation

5.4.1 Flowmeters.

The turbine flowmeters give a pulse count proportional to the liquid flowrate. To enable this signal to be compatible with the monitoring system, a small tachometer circuit has been constructed to give an analog mV signal.

The volumetric flowrate was controlled using a needle valve and kept constant by checking the output from the flowmeter using a digital volt meter. The total volume was collected over a known time interval and measured. The calculated flowrate was compared with the signal from the flowmeter.

The relationship between the measured flowrate and electrical output, for both flowmeters, was found to be linear . These data have been stored in a data file which is accessed during the initialisation routine.

5.4.2 Pumps.

The 3 diaphragm pumps used on the plant were calibrated via the Digital To Analog Converter (DAC) system. Calibration was carried out by varying the air inlet pressure to the pumps and measuring the resultant water flowrate.

In the calibration rig (Fig. 34) the water is pumped to a reservoir to alleviate the fluctuations caused by the mode of operation of the pump. The outlet of the reservoir is connected via a turbine flowmeter to a process vessel where the pressure can be controlled . This gives a measure of the back-pressure on the pump system. The air supply pressure to the pump is set indirectly at the computer. The signal from the DAC is converted, by an I/P converter, to a pressure which is fed to the pump. Measurement of the back-pressure on the system was taken using a digital (QA) pressure calibrator. Logging of air pressure , back-pressure and liquid flowrate enabled pump calibration curves to be produced. A typical set of pump calibration curves is shown in Fig. 35.

5.4.3 Level Gauges.

The apparatus for this consisted of a vertical clear plastic tube connected to the lower tapping of the level gauge. Water was added to the system and the height measured on the plastic tube and compared to the signal given by the intrinsically safe transmitter on the level gauge.

A zero error was evident on the Butane level gauges (for flash and condenser vessels) due to the difference in specific gravity between water and Butane. This has been corrected for in the calibration.

5.4.4 Pressure Transmitters.

The pressure transmitters were calibrated against the QA pressure calibrator using the compressed air system, as shown in Fig. 36.

5.4.5 Pressure Relief Valves.

Using the same system as that for the pressure transmitter, the pressure relief valves were set at a known operating pressure. This was necessary since the relief valves are not designed to operate under normal condition but to operate when an excessive pressure is present. It was decided that the pressure relief valves would be set at 1 bar on the low pressure system and 6 bar on the high pressure system.

Adjustment of the in-line pressure relief valves was by using a lock-nut system adjusted with an Allen key. External adjustable relief valves were set using a spanner on the lock nut system. The only pressure relief valves that will require adjustment during normal operation is that between the compressor and the condenser vessel, which is used to control the pressure of Butane leaving the compressor.

6. SMALL SCALE EXPERIMENTATION.

Small scale experiments were carried out in order that the scale of the pilot plant could be evaluated and also to give an insight into the operation of each of the phenomenon occurring in the process vessels. These experiments were carried out at the Energy Department Research Compound at British Steel, Port Talbot Works.

6.1. Evaporation Trials.

6.1.1. Procedure.

The major problem when carrying out experiments on the evaporation of liquid Butane is to maintain the Butane as liquid until it leaves the outlet of the injection nozzle. Researchers rely on either the use of external cooling of the refrigerant to maintain the low temperature required, or the use of pressure to elevate the boiling point above ambient conditions.

The rig constructed (Fig 37) also utilises the external coolant approach. A metered supply of vapour Butane is passed through two condensers whilst a refrigerated supply of ethylene glycol solution is pumped counter-current to it. The resultant liquid Butane is passed to the injection nozzle.

The warm water or aqueous solution is contained in a clear plastic tube of 100 mm. diameter, the liquid Butane entering at its base. Thermocouples are used to measure the temperature in the vessel. The Butane flowrate, water temperature and anti-freeze temperature were recorded throughout the tests.

To enable photographic analysis of the droplet evaporation, the experiments were repeated using a 100 mm. square glass vessel, thereby eliminating any errors resulting from distortion caused by the curved surface.

The experimentation was carried out using commercial grade Butane at a range of flowrates and two nozzle configurations were tested:-

(i) a single orifice, 1 mm. in diameter.

(ii) a nozzle consisting of 4 orifices, equi-spaced and arranged on a cross, 0.5 mm diameter thus maintaining the same orifice area as in (i).

The temperature of the water in the vessel was monitored, and an assumption was made on the temperature of the Butane being the same as the continuous flow of refrigerated Ethylene Glycol. Pipelines between the condensers and the injection nozzle was kept to a minimum and the pipeline was insulated.

6.1.2. Discussion of Results.

The results show that for the same flowrate, both nozzles performed almost identically. The rate of cooling of the water achieved by both nozzles was the same.

This would indicate that providing that the flowrate is low, both nozzles can achieve 100% evaporation under the same test conditions.

Photographic evidence shows that because the larger nozzle diameter results in the production of the larger droplets, there exists an increase in time and distance above the nozzle before evaporation commences (Figs. 38 & 39). A comparison of these figures shows that the distance above the nozzle is increased by a factor of 3.2 by using the larger nozzle. This would appear to confirm the work of Sideman (50) who predicted a decrease in heat transfer coefficient of a factor of approximately 3, when the bubble diameter is increased from 2 mm. to 3.5 mm., a threefold increase in surface area.

The comparison of evaporation rates against the temperature differential for the two nozzles is shown in Figs. 40 & 41. Here a known volume of water has been cooled under a controlled flow of n-Butane. The rate of cooling can be seen to be identical indicating that complete, or the same degree of, evaporation had been achieved.

Total evaporation of the droplets was achieved, with both nozzles and all the flowrates tested, within 500 mm. of the nozzle tip. The exact position of complete evaporation was difficult to determine because of the turbulence within the system. The water became opaque very quickly during testing, eddies being formed in the water forcing Butane bubbles, or liquid droplets, to the nozzle area. This is considered to be an important phenomenon to be considered in the design of the final system, since it is desirable that the area below the nozzle be free of this turbulence, thus avoiding the possibility of Butane entering the pipeline leaving the Crystalliser.

The high degree of turbulence produced during the evaporation stage also means that the rate of heat transfer is maximised and temperature differentials throughout the body of the fluid are negligible. However, it must be understood that these experiments were carried out in a static column, there being no flow of fluid into or out of the system.

The experiments, therefore, showed that for the flowrates considered in the design of the pilot plant, the evaporation could be achieved effectively at a differential temperature of ~5°C, in the short height available. It was decided that because of the eddies formed during the evaporation process, the nozzle should have a space below it sufficient for the liquid to clarify. This was, at the pilot plant stage to give further problems during the crystallisation trials due to the settling out of the crystals on the base of the crystalliser (Section 7). It was also decided that since at the differential temperatures envisaged in the pilot plant, the pilot plant is effectively operating at a differential temperature of ~8°C, there was a negligible difference in the evaporation rate, the nozzle should incorporate 16 holes of 1 mm. diameter arranged in a circle and on a cross (Fig. 10) fed from a central point.

An attempt was made to test this nozzle under design conditions using a 300 mm square glass vessel approximately 1000 mm long. Problems were encountered on a number of points:

The seal at both ends of the chamber was made by using tie-bars to pull the two ends together onto a neoprene rubber sheet. It was very difficult to ensure that the ends were tightened evenly to avoid seal distortion and the use of the glass vessel resulted in the ends cutting into the rubber seal . This resulted in loss of fluid and inconsistent contact height.

The Butane flow required for the design conditions, could not be achieved using standard commercial grade n-Butane bottles even when several bottles were connected together. This was due to the low pressure in the standard bottles, coupled with the pressure drop in the system. It should be again noted that in order to remove liquid Butane from these bottles they have to be inverted and the liquid removed through standard gas regulators.

During the short duration tests that were carried out it was noted that the turbulence was such that the water became opaque within seconds and that the turbulent eddies went below the nozzle for ~70 mm, it was decided that in the pilot plant the nozzle would be positioned 150 mm above the base and the liquid height would be controlled between 600 and 800 mm. At the end of these short tests there was no evidence of liquid Butane on top of the water, indicating that total evaporation had occurred.

6.2. Separation Trials.

6.2.1. Procedure.

These trials were carried out by placing liquid Butane and Copper (2) Sulphate solution, chosen because of its colour and the possibility of it being used for crystallisation trials in the pilot plant, in a clear sealed plastic vessel.

The vessel was agitated to completely mix the two liquids, and then allowed to stand until separation of the two liquids was achieved. In all tests the separation to a clear, distinct interface was achieved in 24-30 seconds. The results from the tests are shown in Figs. 42 & 43.

5.2.2. Discussion of results.

As can be seen from the photographic record, the top and bottom of the mixture begins to separate at 20 and 6 seconds respectively. Gradually this clarity approaches the centre of the vessel.

At the interface a brown, semi-gelatinous residue is visible, this is believed to be the Mercaptan used to stench the commercial grade Butane.

The original hypothesis about the condensation of Butane in water was that, because there will be turbulence within the fluid, there was a possibility that an emulsion could be formed. This may have been sufficiently stable to require the use of a separation vessel. However, in view of these experiments, some re-design of the pipework between the condenser and separator vessels was undertaken. This will enable fluid to be removed from a point near the top of the condenser as well as the bottom, and fed to the separator where it will be allowed to separate completely.

6.3. Crystallisation Trials.

The principle aim of the project was to develop an energy efficient refrigeration cycle which could be commercially viable. The constraints put on manufacturing industries based on purity of the product requires any crystals formed in the process to be uncontaminated by the refrigerant used. In order to assess the commercial potential of the system it was necessary to carry out tests using some common crystalline products. The aqueous solutions used were of:

(i) Sodium Sulphate Deca-Hydrate.
(ii) Copper (2) Sulphate Penta-Hydrate.
(iii) Iron (2) Sulphate Hepta-Hydrate.

6.3.1 Crystallisation Of Sodium Sulphate Deca-Hydrate.

The objective of the experiment was to crystallise $Na_2SO_4.10H_2O$ by direct heat transfer with liquid Butane. The same apparatus and procedure were used as in Section 6.1.

A saturated solution of $Na_2SO_4.10H_2O$ was prepared at 30°C and liquid Butane bubbled through at 2 l/min. The rig was run for 20-23 min. when crystal formation was observed at about 13°C. The fall in temperature was approximately 1°C/min. Very small crystals were obtained and it was believed that larger crystals could not grow after formation due to the abrasive effect produced by the high turbulence in the vessel.

It was, therefore, decided to repeat the experiment by keeping the Butane flow as low as possible in order to reduce the turbulence produced inside the crystalliser. The difference in size of the crystals formed was investigated by taking samples of the crystals at two separate times.

With the solution initially at 28°C, small crystals were formed at 13°C. A 0.5 litre sample of the crystals was removed and filtered. The temperature of the solution was kept at 13°C (by controlling the Butane flow) and after 15 minutes. another sample was taken out and filtered. These samples were analysed to find any contamination of Butane within the crystals.

The results obtained showed no difference in size of the crystals between the two samples; a colourless crystal was obtained which lost its water of crystallisation when allowed to stand in air, indicating the efflorescent nature of the crystals. For this reasons the crystals were washed in Acetone prior to inspection.

The amount of n-Butane contaminating the crystals was found to be 0.3 $\mu l/g$.

(21×10^{-6} wt %) of crystals for the first sample and 0.1 µl/g (7×10^{-6} wt %.) for the second sample. This quantity of contaminant, equivalent to approximately 3 litres of Butane vapour per tonne of crystals (0.21 gm/tonne.) , is very low and would not cause a problem on an industrial scale. However, a strong odour was evident on the crystals. This was believed to be a result of the stenching agent (Mercaptan) present in the commercial grade Butane being used.

6.3.2. Crystallisation of Copper Sulphate Penta-Hydrate.

The experiments carried out in Section 6.3.1 were repeated using a solution of Copper Sulphate The results were similar in that the crystals formed were finer than those produced commercially by current crystallisation techniques, and again the pungent Mercaptan odour was present. When tested the contamination level was found to be low and would not pose any problems on a production scale.

6.4. Condensation Trials.

A series of experiments has been carried out to investigate the performance of the condenser as well as the conditions required to achieve sufficient condensation of Butane gas. The gas was to be condensed by direct contact with cold liquid.

Instrument grade n-Butane (99.5% pure) which has a boiling point of -0.5°C has been used throughout the tests.

6.4.1. Apparatus.

For the experiments, the apparatus as shown in Fig. 37 was modified to provide a measured inlet vapour Butane flow as shown in Fig. 44.

Three types of nozzles have been used:-

(1) a single hole (1 mm diameter.) nozzle

(2) four hole (0.5 mm diameter.) nozzle (Fig. 45).

(3) eight hole (0.35 mm diameter.) nozzle (Fig. 45).

6.4.2. Procedure.

Initially, cold salt solution at -6°C was used, this was pumped into the condenser to a height of approx. 50 mm. Butane gas was then bubbled through the nozzle at a rate of 2 l/min. The test was allowed to continue until no condensation of gas was observed.

The experiment was then repeated using salt solution which had been cooled to -12°C. Approximately 100% condensation was achieved for the first 10 minutes, the rate of condensation decreasing as the liquid temperature rose until eventually all the gas passed through uncondensed when the temperature reached -0.5°C.

These two experiments proved that direct contact condensation could be achieved using the apparatus. Further experiments were carried out to quantify the condensation rates.

During the subsequent experiments, recordings were made of the Butane flows and the change in liquid temperature. Butane vapour, which condensed , formed a separate layer on top of the solution and the depth was measured with a tape. The readings for the flow in (F1) and flow out (F2), liquid temperature and the depth of the Butane layer were noted every minute.

The above procedure was repeated for gas flows of 1.5 and 1.0 l/min. using the cooled salt solution for each experiment. The experiments were repeated using the other nozzle designs, each time varying the Butane flow from 2.0 to 1.0 l/min. Graphs of percentage condensation vs. temperature of the salt solution were plotted for all the nozzles and comparisons made (Figs. 46 & 47).

6.4.3. Discussion of Results.

6.4.3.1. Effect of Flowrate on Nozzle Performance.

Nozzle 1 (Fig. 46a) : Varying the Butane flowrate from 1 to 2 l/min. had little effect on nozzle performance until the liquid temperature reached -4^{O}C. At this point, the higher flowrates gave 10-15% more condensation than 1 l/min.

Nozzle 2 (Fig. 46b) : The same result was obtained as in Fig. 46a, the lower flowrate consistently achieving a condensation rate 10-15% lower than the others.

Nozzle 3 (Fig. 46c) : The same phenomenon was observed as that seen with the other nozzles. At 1.5 and 2 l/min. the performance of each nozzle was found to be consistent; a much lower "apparent" percentage condensation was achieved for all nozzles at 1 l/min.

The hypothesis is that the layer of liquid Butane formed at the top of the column slowly evaporated due to the absorption of heat from the uninsulated glass walls of the column. As the depth of the liquid Butane layer increases, so does the amount of heat transfer into the system. Consequently a zero error exists for each combination of liquid temperature and liquid Butane depth.

6.4.3.2. Effect of Nozzle Configuration.

Fig. 47, shows that for a constant flowrate , little difference exists between the nozzles. At 1 l/min.,the condensation curves are co-incident, within experimental error, the maximum differential being 8% at any given temperature. The curves also have a similar point at which the percentage condensation decreases rapidly i.e. approximately -1°C.

At a flowrate of 1.5 l/min. the nozzles again produce similar trends. Again a band of approximately 8% covers all 3 curves at all temperatures, but the point at which condensation decreases rapidly is slightly higher at -1.2°C.

At a flowrate of 2 l/min., the performance of the small diameter, multiple hole nozzle (nozzle 3) becomes far inferior; although a condensation rate of 50% was still evident at -1°C. Problems arose in the control of the Butane flowrate for this nozzle, the holes being susceptible to blockage by the salt solution and also due to the high pressure drop through the nozzle system giving rise to inaccuracies in the flow measurement.

6.5 Condensation in Packed Columns.

The previous work showed that total condensation occurred at a Butane flowrate of 2 l/min. within a liquid height of 500 mm.. In order to evaluate and reduce the required height for a given condensation rate at higher flowrates, tests were carried out to assess the suitability and performance of a range of standard packing materials for the condenser performance. It was not considered necessary to test the packings for the crystalliser process because :

(i) the turbulence caused by the evaporation of the refrigerant is sufficient for the crystallisation process.

(ii) the formation of crystals in the packed bed could result in crystal deposition and growth on the packing itself and could result in the formation of large crystalline masses sufficient to cause operation of the condenser to be impossible.

The same experimental rig was used as in Section 6.4. The nozzle used was that of 4 holes each of 0.5 mm. diameter, to give an even distribution at the base of the packed column. The packing was randomly filled, but to enable the effective height of the packing to be used, the packing was supported on a plastic mesh approximately 10mm. above the nozzle.

The condensation rates were measured as previously and the flowrates maintained at 2-4 l/min. The packing designs used were :

(i) 6 mm. Ceramic Raschig Rings.
(ii) 15 mm Ceramic Berl Saddles.
(iii) 15 mm Metal Pall Rings.

The results of all the various configurations are shown in Figs. 48 - 61.

The results obtained show the expected trend for increased bed height and a lower volumetric flowrate towards a higher condensation rate for the same given differential temperature. It should be noted that original testing was carried out using Commercial Grade Butane and some inconsistencies occurred since the composition of this gas varies with prevailing weather conditions, i.e. in colder weather the percentage of n-Propane can increase by a factor of three to maintain a sufficient vapour pressure at low ambient temperatures. The use in this case of Instrument Grade Butane (>99.5% n-Butane) gave a consistent gas composition (with a boiling point of -0.5°C). The addition of insulation to the sides of the vessel also eliminated the effect of ambient conditions on the experiments.

The measurement of such low temperatures gives rise to some error, simply because any inherent zero error is accentuated by the low temperature range required. Also of importance was the criteria that any temperature probe must be as unobtrusive as possible, in order not to significantly affect the condensation pattern. It must also be recognised that the temperature probe must not have too short a response time as variations may occur as bubbles pass the measuring tip. Having considered all these factors and also the paramount constraint of cost, platinum resistance thermometers, of 3 mm diameter were chosen. These give a quoted accuracy of +/- 0.5°C at 0°C. The results are, therefore, susceptible to errors of this level. Over the range of temperatures measured this accounts for up to 10% error. The use of the same instrument, over the same range, however, should minimise these errors and give a good measure of the comparative performances of the packings.

The effect of low packing levels gives some wide variation in performance. The results for Raschig Rings were markedly worse than the other packings at all flowrates. There is no apparent reason for this except that , due to the short packing height, some tracking may have occurred through the bed. The performance at increased bed heights suggests that this phenomena did not occur under these conditions. It may also be due to the increased effect of the mesh and the free space between the nozzle and the mesh. As Sideman (50) showed the condensation in the turbulent area just above the nozzle is much greater than that in lamina conditions because of the increased heat transfer coefficients.

The height of the packing considerably reduces the height required to produce the same condensation levels under the same operating conditions. The effect of using a packing height of 100 mm of Berl Saddles at a Butane flowrate of 4 l/min. is equivalent to obtaining 80% condensation at 2 l/min. for a liquid height of 300 mm., the effective heat transfer rate being increased by a factor of 7.

6.5. Conclusions.

From the results of the small scale experimentation carried out, the following conclusions have been drawn :-

(i) The evaporation of liquid Butane in warm water is very efficient due to the high degree of mixing resulting from the high increase in volume of the butane (1 volume of liquid giving rise to ~200 volumes of vapour).

(ii) The evaporation can be controlled to maintain a given temperature in the evaporator.

(iii) The crystals produced are unlikely to be large, possibly due to the abrasion resulting from the high turbulence existing in the evaporator. Another factor that is highly influential is the rate of cooling. The absence of a significant temperature differential in the evaporator gives rapid cooling which is not conducive to the formation and growth of large crystals.

(iv) The Butane can be condensed completely using a 0.5 mm. diameter nozzle providing that the difference in temperature between the cold liquid and the Butane boiling point is at least 5°C; and the depth of the liquid above the nozzle is approximately 500 mm.

(v) Contamination of the crystals produced during the evaporation trials showed a maximum Butane level of 0.3 μl/g of crystals. equating this to a full scale plant, the butane loss would be a maximum of 0.3 l/tonne of crystals. Although this does not seem unduly high, the losses on a weeks' operation would be approximately 17 kg.

(vi) Condensation using a packed bed can greatly increase the rate of heat transfer, and therefore, reduce the size of the Condenser considerably.

7. PILOT PLANT OPERATION

Commissioning and troubleshooting of the system was carried out using water and commercial grade Butane as the process fluids. A number of difficulties were encountered and alterations to the proposed mode of operation of the system were necessary to alleviate these difficulties.

A view of the pilot plant is shown in Fig. 62.

The tests carried out on the pilot plant can be categorised as follows:

(a) tests utilising a Butane / water system, primarily to enable the plant to be commissioned and to establish that the plant could be operated safely and for long periods.

(b) tests utilising a Butane / water system to establish the effect of process variables (i.e. pressure, temperature and flowrate) on plant performance.

(c) tests utilising a Butane / Iron (2) Sulphate solution system, to establish the rate of crystal formation in the crystalliser, and the purity and the size distribution of the crystals.

(d) tests utilising a Butane / waste pickle liquor system, in order to simulate an actual acid recovery scenario. This enabled direct comparison with the crystals formed by the Lurgi Acid Recovery Process.

(e) tests utilising a Butane / Copper (2) Sulphate solution, repeating the test of (c), this again enabled a direct comparison with commercially available (General Purpose Reagent) crystals.

In order to monitor the system temperature, pressure, flow and level, suitable instrumentation was installed on the pilot plant. The data were collected using two Thinklab units acting as analog-to-digital and digital-to-analog converters linked to a PC. The data collected during each scanning of the variables were saved in a data file for each test. Each scan was displayed on a VDU so that the operator could instigate any adjustments of the system.

7.1 Butane / Water System

The tests carried out on this system constituted the major portion of the large scale experimental work. The aim of this work was to:-

(i) carry out commissioning trials.

(ii) undertake measurement of process variables, and their effect on plant performance.

7.1.1 Commissioning Trials

7.1.1.1 Start-up Procedures

During the commissioning programme failures were experienced in both the stainless steel non-return valves and diaphragms of the Butane compressor. Discussions with the manufacturers highlighted the existing start-up procedure as being the probable cause of the failures. The compressor was not capable of start-up with either a positive inlet or back pressure without modification of the compressor heads. As this necessitated the return of the unit to the manufacturer in Germany, it was decided that a modification of the start-up procedure would be preferable.

To enable the inlet Butane pressure to be as low as possible it was decided to start the compressor with the vent valve on the crystalliser open to atmosphere. The back-pressure was minimised by opening the vent valve on the condenser. Further difficulties were encountered with water flowing from the condenser into the compressor prior to start-up and after shut-down. This problem was prevented by the installation of a low pressure activated (0.2 bar) non-return valve between the compressor outlet and the condenser.

As soon as the system was purged thoroughly, both vent valves were closed and the system operated normally.

A safety feature of the chosen compressor was the use of flexible drive couplings, which protected the drive motor from adverse and probably damaging conditions. However, the cost of this failure was to disable the pilot plant until the couplings were replaced, not an expensive item but only available from the German manufacturers and, therefore, time consuming.

7.1.1.2 Flow control.

The pumps chosen for the pilot plant were air actuated diaphragm pumps, suitable for operation in hazardous areas, with hazardous fluids and at pressures up to 6 bar gauge. Unfortunately due to their design they are susceptible to flow fluctuations caused by a change in either air supply pressure or back pressure of the system.

With both the crystalliser pressure and condenser pressure varying constantly, it proved impossible to control the flow of water into and out of the crystalliser accurately. However, by modifying the air venturis on the pumps it was possible to control the flowrates within limits that enabled the liquid levels in the crystalliser to be controlled within a 100 mm band.

The pumps are specifically transfer pumps, i.e. used to transfer material from one vessel to another at a slightly higher pressure. In the design of the system, it was envisaged that there would be little or no pressure differential between the flash and crystalliser vessels, however, in practice a substantial pressure differential, frequently >1.0 bar existed. The result was that the pump control setting had no effect on the flow of liquid Butane into the crystalliser. This was due to the pressure difference across the pump being too high, the liquid n-Butane pressure in the Flash vessel forcing the liquid past the diaphragm of the pump. Control of the flowrate could only be effected by the manual manipulation of valves in the liquid Butane supply line. Control of the Butane flowrate was a function of:-

(i) the temperature in the crystalliser
(ii) the pressure in the crystalliser
and (iii) the differential pressure between the flash and crystalliser vessels.

The lack of flow measurement between the crystalliser and condenser vessels gave rise to a great reliance on the control of the liquid level in the crystalliser. This was difficult to achieve because of the problem of balancing two pumps with inlet and outlet pressures varying continuously.

The pumps had been calibrated assuming that a variation of inlet pressure would have little or no effect on throughput. This was found to be incorrect, the liquid Butane transfer pump passed sufficient Butane for the operation of the crystalliser even when shut down and the crystalliser-condenser transfer pump gave flows in excess of those predicted from calibration tests.

With the reliance on pressure differentials to control the flow of liquid Butane into the crystalliser, it proved beneficial to eliminate the venting of the vapour from the flash vessel to the condenser, thus maintaining the pressure in the flash vessel at approximately 1 bar gauge. This also had the added advantage of ensuring that the Butane evaporated in the crystalliser was the same as that compressed and passed to the condenser.

A further benefit resulting from this modification was the maintenance of a positive pressure in both the flash and crystalliser vessels, thus eliminating the possibility of freezing the water.

The control of liquid Butane flow from the separator to the flash unit was carried out by the operation of the solenoid valves in the delivery line. One valve was operated as a direct result of the activation of the level switch at the top of the separator. The result of this action was to transfer liquid Butane from the separator vessel, which was replaced by fluid from the condenser.

Consequently, the level of the Butane / water interface rose slowly. Care was exercised in not allowing the interface to reach the level of the Butane offtake, as this had resulted in the transfer of water into the flash and subsequently into the Butane pipework during earlier tests. This resulted in premature evaporation of the Butane causing ice formation and blocking of the pipework between the flash and crystalliser vessels.

The transfer of the Butane / water mixture from the condenser to the separator proved difficult due to the small pressure differential between the units and also because some separation was taking place in the condenser. Operation of the system with only the original bottom offtake in the condenser resulted in the transfer of nearly pure water to the separator, whilst the condenser gradually filled with liquid Butane. To overcome this a second offtake was installed approximately 300 mm. from the top of the vessel. During the initial 10-20 min. of each test, both these offtakes were closed. As soon as the liquid level in the condenser reached the top offtake, this was opened. For the majority of the test period, this was sufficient to maintain conditions in the condenser at a relatively steady state. However, some instances did occur when the interface level in the separator dropped to its minimum permitted level, and the bottom offtake on the condenser was opened to transfer water to the separator.

7.1.1.3 Water Flow Control

The flow of water into and out of the pilot plant was measured by two pre-calibrated flowmeters. The pump used for transferring the water from the storage tanks to the crystalliser was the only one that was not subject to variations in supply pressure and consequently it was capable of being easily controlled.

The outlet flowrate from the separator was controlled by using a manual needle valve situated within easy reach of the computer operator. The flow out of the system was adjusted to match that entering the system, but occasionally the flow was altered to take into account fluctuations in separator interface levels.

7.1.1.4 Compressor Control

The compressor was, without the adoption of a phase frequency controller, very difficult to control. The output pressure from the unit was subject to fluctuation, a variation in inlet pressure having a seemingly disproportionate effect on the outlet pressure. The pressure in the system increased quickly (~7 min.) to 2 bar gauge, and then more slowly to give a system pressure of 3 bar after ~40 min. and 3.5 bar after ~60 min. (Fig. 63).

Due to this slow increase in pressure it was decided that the best form of operation was to allow the compressor to find its own operating conditions. The continuous monitoring and recording of the system variables has given the possibility of analysing the operation of the pilot plant at various conditions throughout the tests.

7.1.2 Normal Operation Water / Butane System

The operation of the pilot plant with the Butane / water system proved to be very important in preparation for the more demanding trials utilising crystallisation. The data collected were stored in a data file and could be plotted following the completion of the test. Graphical representation of one such test is shown in Figs. 64-67. Fig. 68 shows a typical VDU display and the statistical analysis of the data collected during the same test is shown in Fig. 69 .

As can be seen from Fig. 66, the crystalliser temperature shows some fluctuation around the desired temperature of 6°C, whilst the crystalliser pressure varies with the operation of the solenoid valve between the separator and flash vessels.

Incoming water temperature gradually increases with time, this was a function of the temperature of the water returning from the separator and hysteresis in the temperature controller. As a result of this the flow of water into the crystalliser had to be controlled to maintain the desired conditions. Later tests were carried out with the water from the separator being passed to drain, thus maintaining a fairly constant water temperature.

Temperatures measured within the condenser show little variation in the bottom temperatures, but the top two sensors indicate consistently lower temperatures. This is indicative of a change in fluid from a water / Butane vapour mixture to a Butane liquid / Butane vapour mixture. This enabled the presence of an interfacial area to be predicted with good accuracy (+/- 50 mm.). This phenomenon can be seen more clearly with reference to Fig. 67. Initially the bottom 7 sensors form a band approximately 4°C above the other 2 sensors, by allowing the level of the interfacial area to rise and fall it can be seen that individual sensors move sequentially between the two temperature ranges, indicating the movement of the Butane / water interface past the sensors.

The difference in temperature between the top and bottom of the condenser was consistently ~ 4°C, with the incoming Butane vapour ~3°C above the bottom temperature.

The pressure differential between the condenser and separator vessels was ~ 0.4 bar under normal conditions, a larger differential occurring when Butane was being transferred to the flash vessel. Temperature differential between the top and bottom of the separator gradually decreased until a minimum differential of 3°C was reached. The temperature differentials of the two components measured between the condenser and separator vessels were 3°C for the water and 2°C for the Butane.

The maintenance of a high pressure (>1 bar gauge)in the flash vessel ensured sufficient flow of Butane into the crystalliser, but gave rise to lack of control of the flowrate by using the in-line Butane pump. For later trials this was dispensed with.

A statistical analysis of this test is shown in Fig. 69.

Compressor faults provided an opportunity to carry out tests with the compressor operating at approximately 50% efficiency. The results of this test are shown in Figs. 70-74. Similar characteristics are shown to the test discussed above but with lower pressures and consequently temperatures in the condenser system.

7.1.3 Oxygen Levels in the Condenser

One of the major safety considerations highlighted by the HAZOP study and discussions with the Health and Safety Executive and LPG suppliers was that of possible oxygen build-up in the system.

The most likely location for any oxygen to separate and remain was believed to be at the top of the condenser. Here the cold process fluid was heated through approximately 35°C, resulting in a decrease in oxygen solubility and the possible release of oxygen into the vapour. This would not be applicable to a closed loop because any Oxygen dissolved in the water at the inlet temperature would be less than the saturation level at the condenser because of the lower temperature in the condenser. However, the system used for the crystallisation tests necessitated the cold crystal laden liquor from the crystalliser to pass through a fine, open filter bag to remove the crystals. The cascade of liquor into the storage tank under the filter is likely to aerate the liquor prior to being pumped to the condenser. Also, any oxygen introduced into the system at any of the air actuated diaphragm pumps would eventually find its way into the condenser.

Samples were taken from the top of the condenser throughout a number of the longer tests. At each sampling time, three samples were taken and analysed using a "Testoterm" gas analyser, which utilises a chemical cell for oxygen determination. To eliminate any effect Butane might have on the cell output, calibration measurements were undertaken using 99.5% pure n-Butane.

The analyses showed that a small quantity of oxygen was present in the gas samples, the first sample taken having considerably more oxygen than later samples(Table 3) reaching a maximum of 2% but dropping to 0.1% for the third sample. This indicated that stratification was taking place at the top of the vessel, as expected due to the differential in density between the oxygen and vapour n-Butane.

With the present plant configuration it was not possible to continuously monitor the oxygen build-up.

7.2 Operation with Aqueous Iron (2) Sulphate

The first of the crystallisation tests carried out was on aqueous Iron (2) Sulphate. A solution was prepared by dissolving Iron (2) sulphate crystals in water until a solution, which would be saturated at 20°C was obtained. The test was carried out in exactly the same way as for water except for a modification in the pipeline between the crystalliser and condenser vessels. This was the installation of a filtration system to remove the crystals formed and a storage tank to maintain a supply for the condenser.

Samples of the liquor were taken periodically during the test at the exit of the filter. It was found that the filter pore diameter of 50 microns was too large to effectively remove the fine crystals formed but a finer filter would have created too great a liquid hold-up to be practicable. For the purpose of analysis samples of the liquor from the filter were re-filtered and the resultant liquor was analysed to determine the sulphate concentration. Samples of liquor prior to the filter were treated in the same way to obtain crystal samples which were analysed for contamination by the Butane and also photographed to show both crystal shape and size.

The results of the crystal and liquor analyses are shown in Table 4.

The crystals showed very little evidence of contamination with the Butane, although they exhibited the characteristic smell of the Mercaptan used to stench the commercial grade Butane. The Butane levels of 0.2-1.7 μl/g do not pose any safety problem, and although it is believed that this Butane is associated with the wetness of the crystals and not the crystals themselves it is proposed that future work could be aimed at investigating the mode of contamination of the crystals. An efficient centrifuge or crystal separator may alleviate this contamination.

Comparison between the crystals as supplied, the product of a Lurgi acid recovery plant, can be made by comparing the photographs (Fig. 75). These show that the crystals produced are a factor of 4 smaller than those supplied, indicating the effect of the rapid cooling produced in the crystalliser.

7.3 Operation with Aqueous Copper (2) Sulphate

An aqueous solution of Copper (2) Sulphate was prepared, using commercial crystals, which was saturated at 32°C. This was treated in the same way as the Iron (2) Sulphate in 7.2.

The results of the crystal and liquor analysis (Table 5) show similar results to those of the Iron (2) sulphate. The crystals produced were very fine and consequently much paler than the original crystals. Fig. 76, shows the size distribution of a sample of the crystals.

7.4 Operation with Waste Sulphuric Acid Pickle Liquor

The final liquor to be treated in the pilot plant was a waste pickle liquor, taken from a point at the entry to the Lurgi acid recovery plant and transported to the pilot plant in 45 l containers.

The pilot plant was operated in the normal manner with samples of liquor and crystals taken periodically.

Difficulty was experienced in maintaining the required flow out of the crystalliser due to the formation of large quantities of crystal resulting in the blockage of the pipework. Pipes were removed and cleared manually to enable the samples to be taken. This cannot be done on a large scale plant but direct contact crystallisers e.g. Swenson DTB, are available to overcome this problem.

The liquor and crystal analyses are shown in Table 6. The results showed a 25 % reduction in the iron content and a slight increase of 0.4 % in the acid strength. This was less than that achieved by the existing Lurgi plant principally because the acid supplied was:

(a) before the precoolers

(b) the only water removed from the pilot plant was the water of crystallisation of the crystals, compared with the removal of water vapour and water of crystallisation in the existing vacuum chilling

(c) concentrated Sulphuric Acid (BOV) is added to the crystal slurry to enhance the crystallisation prior to separation.

Butane contamination was again low and well within acceptable limits. Photographs of the crystals are shown in Fig. 77

7.5 Conclusions

The tests have shown that the principles upon which the Semi-Open Refrigeration Cycle are based can be linked in a continuous plant.

The crystals obtained from the system have been shown to be only slightly contaminated with Butane and it is suggested that further work be carried out to investigate the mode of this contamination.

The crystals formed have proved to be very small in comparison with the as supplied crystal. This is probably due to two causes:

(i) The solution is subjected to an almost instantaneous drop in temperature of ~40°C, a high chilling rate being indicative of the formation of small crystals.

(ii) The crystalliser is highly turbulent, possibly resulting in abrasion reducing the capability of the crystals growing.

The condenser vessel exhibited the performance predicted by the small scale experimentation, complete condensation taking place in the height available above the nozzle, and separation of the two liquids also occurring due to the residence time in the condenser. This would give scope in the further development of the system to dispense with the separator vessel.

The overall efficiency of the system, based on water / solution temperature into and out of the system was ~80%. If the separator vessel was to be removed, the overall efficiency would rise to ~90%, approaching the figures of Jenkins (11).

Further development of the control system is required, in particular the control of n-Butane flows.

8. CONCLUSIONS.

The principle aim of the research, as stated earlier, was to design, construct and commission a plant based on a Semi-Open Refrigeration Cycle capable of producing crystals, of a number of commercial inorganic salts, at the required quality. From this point of view the work has been totally successful. However, this must be considered only as a first step in the design of a commercially viable SORC plant.

The research carried out has confirmed the following points:

(i) Evaporation of liquid Butane in water or inorganic solution occurs at such a rate that the total evaporation of the refrigerant occurs within a short distance from the injection nozzle.

(ii) The effect of nozzle diameter on the evaporation rate was not significant over the range of nozzle diameters considered.

(iii) The height of liquid above the nozzle was of importance since at low levels it was possible for liquid Butane droplets to reach the surface before complete evaporation occurred, a liquid Butane layer being noted on top of the water at the cessation of trials.

(iv) Possibly one of the most interesting points to be observed during the evaporation trial was the setting up of eddies which on occasion extended to the area below the nozzle. This was considered to be of importance in the design of the pilot plant where liquid/crystal slurry was removed at a point just below the injection point. The presence of any liquid Butane in the stream leaving the crystalliser would result in pump failure and/or Butane leakage.

(v) Separation of the two components, which was considered at the outset to be a possible problem, occurred very quickly. The separation occurring in the condenser was not considered sufficient for the continuation of the cycle. However, it should have been possible, without time and financial constraints to have redesigned the condenser in such a way that the services of the separator could be dispensed with.

(vi) The evaporation of liquid Butane in warm water is very efficient due to the high degree of mixing resulting from the high increase in volume of the Butane (1 volume of liquid giving rise to ~200 volumes of vapour).

(vii) The evaporation can be controlled to maintain a given temperature in the evaporator.

(viii) The crystals produced are unlikely to be large, possibly due to the abrasion resulting from the high turbulence existing in the evaporator. Another factor that is highly influential is the rate of cooling. The absence of a significant temperature differential in the evaporator gives rapid cooling which is not conducive to the formation and growth of large crystals.

(ix) The Butane can be condensed completely using a 0.5 mm. diameter nozzle providing that the difference in temperature between the cold liquid and the Butane boiling point is at least 5°C; and the depth of the liquid above the nozzle is approximately 500 mm.

(x) Contamination of the crystals produced during the crystallisation trials showed a maximum Butane level of 0.3 μl/g of crystals. Equating this to a full scale plant, the Butane loss would be a maximum of 0.3 l/tonne of crystals. Although this does not seem unduly high, the losses on a weeks' operation would be approximately 17 kg of n-Butane.

(xi) Condensation using a packed bed can greatly increase the rate of heat transfer, and therefore, reduce the size of the Condenser considerably.

The Safety studies on the pilot plant gave the following conclusions:

(xii) The HAZOP study and Dow Fire and Explosion Index indicated that the number of potential hazards involved with the S.O.R.C was high, but that sufficient safety measures and safe operating practices could be undertaken to eliminate or reduce those hazards.

(xii) Operation of the pilot plant using level gauge control was found to be an integral part of the safety system; which justified the high capital expenditure on these items.

(xiii) The other extensive safety measures; including the Butane sensors/alarms, Zener barriers, pressure relief valves, and high working pressure fittings; have also been justified, in the light of the hazards identified.

(xiv) The HAZAN has shown that due to the extensive safety back-up systems; installed for the safe control and operation of the pilot plant in order to prevent a potentially dangerous leak of explosive material and/or an ignition source occurring; the likelihood of an incident occurring was very low, at once in 38 years. This is acceptable for a pilot plant of short experimental life but before a production plant could be built the tree should be studied in depth to indicate the areas that should be improved upon in order to improve safety.

The conclusions drawn from the pilot plant trials are:

(xv) The crystals obtained from the system have been shown to be only slightly contaminated with Butane and it is suggested that further work be carried out to investigate the mode of this contamination.

(xvi) The crystals formed have proved to be very small in comparison with the "as supplied" crystal. This is probably due to two causes:

(a) The solution is subjected to an almost instantaneous drop in temperature of ~40°C, a high chilling rate being indicative of the formation of small crystals.

(b) The crystalliser is highly turbulent, possibly resulting in abrasion reducing the capability of the crystals growing.

(xvii) The condenser vessel exhibited the performance predicted by the small scale experimentation, complete condensation taking place in the height available above the nozzle, and separation of the two liquids also occurring due to the residence time in the condenser. This would give scope in the further development of the system to dispense with the separator vessel.

(xviii) The overall efficiency of the system, based on water / solution temperature into and out of the system was ~80%. If the separator vessel was to be removed the overall efficiency would rise to ~90%, approaching the figures of Jenkins (11).

(xix) Further development of the control system is required, in particular the control of n-Butane flows.

9. RECOMMENDATIONS FOR FUTURE WORK

The work carried out in this project has highlighted several topics that need to be addressed if the concept is to be developed further. The work has proven that the principles upon which the concept is based are capable of being achieved and inter-linked to form a continuous process. The foundation work has been completed and it is believed that work in the following areas could prove both enlightening and beneficial:

The work of Lench (25) has resulted in the development of a model for the evaporation of a single droplet, iso-Pentane in water. In a process this would not be the case, multiple bubble trains would be the norm. My own small scale experiments (Section 6) have shown that, with multiple bubble trains, the turbulence in the vessel appears to result in the setting-up of eddy currents almost to the base of the vessel. The adaptation of the model proposed by Lench to a system of multiple interacting bubble trains would prove interesting in respect of the understanding of industrial scale equipment.

The contamination of the crystals with the n-Butane is low but still must give some cause for concern. It is not known from the tests, to date, what is the exact nature of the contamination. A detailed study of the crystal structure would indicate whether the contamination is on the crystal surface, encapsulated within the crystal structure or associated with the water of crystallisation. It has been reported that a hybrid is also formed between n-Butane and water and this may play a significant part in the contamination of the crystals and this also should be investigated.

Condensation of the n-Butane vapour in packed beds has been shown to substantially increase the rate of heat transfer and further work utilising multiple nozzles and various packings should be undertaken to evaluate the effect the packing has on the heat transfer mechanisms taking place.

The applications of the process within British Steel is limited, steel pickling now being carried out preferentially by Hydrochloric Acid which has been found to give an improved steel surface after pickling. Commercial exploitation of the process, however, should be considered for the production of various chemicals, both inorganic and organic, for use in the Chemical industry.

The pilot plant has operated with computer monitoring and operator/computer control. A further development would be the complete automation of the process coupled with a scale-up to industrial scale. The thermal efficiency of the process has only been approached simplistically due to the operational difficulties, however, further work should be aimed at the optimisation of the efficiency of the process.

The condensation of individual bubbles has been studied by other authors but, to my knowledge, few have approached the problem of counter-current flow and heat transfer in systems incorporating multi-nozzle injection with interacting bubble/droplet streams. The effect of the various parameters of such a system would prove challenging to the most gifted of researchers.

NOMENCLATURE

a	Diffusion coefficient.
b	Property parameter (Wanchoo and Raina (45)).
C	Constants as defined.
C_F	Parameter Fair(22).
Cp	Heat capacity.
D	Mass diffusivity, bubble / drop diameter.
d	Diameter, surface mean diameter of drop.
D_L	Correction factor (Wanchoo and Raina (45)).
f_1	Viscosity factor, $(\mu_l / 2.42)^{0.16}$.
f_2	Density factor, $(62.4 / \rho_l)^{1.25}$.
f_3	Surface tension factor, $(72.8 / \sigma)^{0.8}$.
G	Gas mass velocity.
H	Height of a transfer unit.
h	Heat transfer coefficient, height (h).
I(A)	Integral as defined (Wanchoo and Raina (45)).
K	Thermal conductivity.
K_v	Velocity factor (Sideman (50)).
k	Mass transfer coefficient.
L	Liquid mass velocity.
m	Ratio of liquid to vapour density in the bubble, exponent as defined by Fair(22)
n	Exponent as defined by Fair(22)
p	Pressure.

q	Overall heat transfer coefficient.
R	Radius of two phase bubble.
T	Temperature.
t	Contact time.
U,u	Rise velocity of bubble.
x	Weight percent of vapour in the bubble.

α	Thermal diffusivity.
β	Angle as defined in Fig. 6., dimensionless radius (Sideman(50)).
β_s	Angle of separation.
Δ	Differential.
δ	Film thickness.
Φ	Liquid phase parameter (Fair(22)).
γ	Dimensionless time for stagnant bubble given by $Ja'Re^{0.5}Fo$.
λ	Latent heat of vaporization.
μ	Viscosity.
θ	Polar angle , temperature of phase.
ρ	Density.
σ	Surface tension at interface.
ψ	Tower parameter relating to degree of flooding (Fair(22)).
∞	Bulk condition.

Dimensionless Groups:

Fo	Fourier No.	$\alpha t / R_i^2$
Ja	Jacob No.	$Cp_l \Delta T / \lambda$
Ja'	Jacob No. (modified)	$\rho_l Cp_l (Ts - T\infty) / \lambda \rho_v$
Nu	Nusselt No.	$h_c d/K$.
Pe	Peclet No.	ud / α.
Pr	Prandtl No.	$Cp\mu_c / K$
Ra	Rayleigh No.	$D^3 g \Delta\rho / \mu_c a_c$.
Re	Reynolds No.	$ud\rho / \mu$.
Sc	Schmidt No.	$\mu_c / \rho_c a_c$.

Subscripts

c	continuous phase.
d	dispersed phase.
F	Function.
g	gaseous.
i	initial conditions.
l	liquid.
o	equilibrium conditions.
t	at time (t).
v	vapour phase.

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APPENDIX 1

Hazard and Operability Study (HAZOP)

Apparatus: Crystalliser - Reduce acid temperature to 6°C to facilitate the crystallisation of Iron (2) Sulphate			
Line Number : 1			
Intention : Supply of acid (at 20% Sulphuric Acid and 50°C)			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Flow	Line blockage before and after pump or pump failure.	Acid levels in the crystalliser would fall to leave the unit full of n-Butane. Fail-safe level control would automatically shut-down the system if the liquid level falls below the operating limits.
No	Temperature	Thermocouple fault.	Check thermocouple.
No	Pressure	Pump failure or Line blockage.	As for no flow.
More	Flow	Pump fault. Compressed air flow/pressure high.	High acid flow into unit, resulting in overflow to compressor and possible catastrophic failure. Level gauge control would result in a fail-safe shut-down procedure.
More	Temperature	Immersion heater or thermostat fault.	Maximum temperature of 100°C, therefore, no serious consequences. The level may rise in the unit due to the increased amount of cooling required but level control would be employed.
More	Pressure	Pump fault.	The diaphragm pump gives a lower flow than required at higher pressure. Level gauge control would be used.
Continued.....			

Apparatus: Crystalliser - Reduce acid temperature to 6°C to facilitate the crystallisation of Iron (2) Sulphate

Line Number : 1

Intention : Supply of acid (at 20% Sulphuric Acid and 50°C)

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
Less	Flow	Line blockage or pump fault. Leak.	Low acid liquid level in the crystalliser. Level gauge control would prevent Butane from leaving the vessel . Any acid leak would be visible. All equipment will be stainless steel, acid resistant.
Less	Temperature	Thermostat fault.	Check thermostat.
Less	Pressure	Pump fault or line blockage. Leak.	More flow would result from the diaphragm pump which would then be controlled by the level gauge. As previous, visible leak and acid resistant equipment.
Reverse	Flow	Blockage of outlets, possible liquid level too high in the unit.	Acid supply pump acts as a non-return valve. Check level gauge operation.

Apparatus: Crystalliser.

Line Number : 2

Intention : Liquid Butane feed to the Crystalliser from the flash vessel

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Flow	No Butane in flash unit, pump failure or blockage.	No change would occur in the Crystalliser temperature. Automatic fail-safe shut-down would then occur if the flow control on the acid flow had no effect.
		Leak	Possible explosion hazard-Butane sensors would give an audible warning at 20% of the Lower Explosion Limit (LEL) and instigate the fail-safe automatic shut-down procedure at 40% LEL.
More	Flow	Pump fault	Flash unit could be emptied of liquid Butane, leaving vapour in the flash vessel - increasing the possibility of explosion. The cooling effect on the acid would be increased and ice could be formed causing possible blockage and rupture of pipework and connection failure. Temperature control of the crystalliser would be used to control the acid and Butane feeds. High pressure pipework and compression fittings would minimise the possibility of pipe rupture or connection failure.
More	Temperature	Insufficient chilling at the Flash vessel or pump fault.	Possible vaporisation and expansion in the pipeline. The use of stainless steel, high working pressure fittings will minimise the possibility of rupture or failure. Temperature control from the Crystalliser will be used on the Butane feed.

Continued.....

Apparatus: Crystalliser.			
Line Number : 2			
Intention : Liquid Butane feed to the Crystalliser from the flash vessel			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Pressure	Partial blockage of line downstream.	Build-up of working pressure - use of high working pressure fittings will minimise the consequences. Diaphragm pump will give constant pressure regardless of Flash unit operation, but will give a lower flow, reliance again on temperature control.
		Fully blocked or pump failure.	Pump shut-off due excessive back-pressure. Temperature rise in Crystalliser will result in fail-safe shut -down procedure. Excessive pressure in either the Flash or Crystalliser units will be catered for by the installation of pressure relief valves.

Apparatus: Crystalliser

Line Number : 3

Intention : Acid and Iron (2) Sulphate crystal feed to the centrifuge/separator.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Flow	No liquid in the Crystalliser, level gauge fault or blockage.	Abnormal flowmeter reading - automatic shutdown. Level control from unit.
Less	Temperature	Excess Butane flow to the Crystalliser or low acid temperature/flow	Ice could be formed. Use of n-Butane minimises this risk.
Less	Pressure	Failure of both supply pumps to the Crystalliser.	Butane vapour could flow back into the Crystalliser. The only common mode of pump failure is compressed air failure, in which case the downstream pump will also fail. Level control would then be implemented in the Condenser and Crystalliser. A "flag" will be evident on the control computer indicating the presence of a high/low pressure.
Reverse	Flow	Common mode failure of both feed pumps and downstream pump.	Reverse flow would occur in the Butane line until automatic shut-down occurred at the Crystalliser due to liquid level control at lower limit of liquid level.

<table>
<tr><td colspan="4">Apparatus: Crystalliser</td></tr>
<tr><td colspan="4">Line Number : 4</td></tr>
<tr><td colspan="4">Intention : Butane vapour exit to compressor after evaporation.</td></tr>
<tr><th>Guide Word</th><th>Possible Deviation</th><th>Possible Cause</th><th>Consequences and Action</th></tr>
<tr><td>No</td><td>Flow</td><td>No Butane feed to Crystalliser
or
blockage
or
no suction from upstream compressor
or leak</td><td>Less Butane feed to Condenser, loss of pressure in the flash vessel, level gauge and pressure transmitter indication in Flash vessel..
Temperature control in the Crystalliser resulting in safe shut-down.
Vapour leak detected by Butane sensors - resulting in audible alarm followed by automatic safe shut-down procedure.</td></tr>
<tr><td>More</td><td>Temperature</td><td></td><td>Irregular temperatures at acid exit due to the high pressures.
High pressure "flag" on computer with pressure relief valve operating and finally initialisation of automatic safe shut-down procedures.</td></tr>
</table>

Apparatus: Crystalliser

Line Number : Unit

Intention : Reduce acid temperature to $6^{\circ}C$ to facilitate crystallisation of Iron (2) Sulphate.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Power	Loss of 110/240 V supply.	Automatic fail-safe shut-down if power fails, also manual "panic" button shutdown available.
No	Mixing	No Butane feed.	Temperature control leading to safe automatic shut-down.
No	Level gauge control	Mechanical fault	No signal would give an automatic fail-safe shutdown as with a max./min. level of acceptance on the signal. The level gauge system is such that a flooded float would sink. As the Butane would always be above the acid, automatic shut-down would occur before any Butane could drain out through the acid outlet.
No	Compressed air	Air compressor fault or blockage.	No compressed air would result in the shut down of all pumps and air actuated valves would fail-safe to closed as in automatic fail-safe mode.
More / Less	Mixing	More / less turbulence. Higher / lower flows.	Temperature control would initiate automatic fail-safe shutdown.
More / Less	Compressed air pressure	Air compressor fault .	Alteration in pump performance resulting in abnormal level/flow readings leading to automatic fail-safe shutdown.

Continued.....

Apparatus: Crystalliser

Line Number : Unit

Intention : Reduce acid temperature to 6°C to facilitate crystallisation of Iron (2) Sulphate.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More / Less	Butane concentration	Less / more acid flow or Butane metering pump fault.	Fall or rise in levels resulting in level control. Change in vessel pressure leading to pressure control possibly via pressure relief valves. Vessels protected with Butane/acid resistant material coating.
More	Flow	Loss of control at Crystalliser.	Action at Crystalliser, flow control downstream
High	Acid concentration	Loss of control at Crystalliser or Acid feed concentration high.	Acid resistant lining to unit.

Apparatus: Crystalliser

Line Number : Unit

Intention : Separation of Iron (2) Sulphate from acid stream

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Flow	Loss of control at Crystalliser	Action at Crystalliser, flow control downstream.
High	Acid Concentration	Loss of control at Crystalliser or Acid feed concentration high.	Action at Crystalliser, use of acid resistant equipment alleviates hazard.

Apparatus: Condenser : Condense Butane vapour by direct contact with a cold acid stream.

Line Number : 5

Intention : Butane vapour supply line

Guide Word	Possible Deviation	Possible Cause	Consequences and Action
More	Flow	Compressor fault	Increased level in Condenser initiating level control, incomplete condensation resulting in a build-up of vapour. Pressure and temperature would increase but monitoring / control would eliminate the hazard.
More	Pressure	Compressor fault	Pipes / fittings have a Safe Working Pressure of 100 times the operating pressure whilst the maximum pressure rating of the compressor is only 6 bar gauge.
Less	Flow	Compressor fault or vapour Butane supply to compressor is low	Possible evacuation of Flash and Condenser vessels by compressor. Low level gauge control and low pressure automatic shutdown instigated at the Flash or Condenser.

Apparatus: Condenser			
Line Number : 6			
Intention : Acid supply line at 6°C used to condense Butane vapour to liquid.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Temperature	Pump fault or Loss of control at Crystalliser or Butane supply to Crystalliser has failed.	Increased temperature at the Condenser, less condensation of Butane, build-up of vapour pressure and temperature - prevented by computer control and safe shutdown procedures.

Apparatus: Condenser			
Line Number : 7			
Intention : Acid / Butane liquid feed to separator.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Flow	More acid / Butane supply flow	Flowmeter and level control of feed flows will prevent any incident occurring.
Less	Temperature	Condenser temperature is low. either: excess acid flow from centrifuge or low Butane flow from compressor.	Temperature measurement will give control on Condenser; linked to flow control of acid and constant volume output of Butane from compressor.

Apparatus: Condenser

Line Number : Unit

Intention : Condense Butane vapour by direct contact with cold acid stream.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More / Less	Mixing	Higher / lower supply flows.	More / less intimate contact - condensation more / less likely. If less condensation occurs there is a possibility of vapour build-up: flow, temperature, pressure and level control would be required to compensate.
More	Butane concentration in vessel.	Acid / Butane supply fault.	Incomplete condensation of Butane, build-up of vapour, temperature, pressure and level control required.
Less	Butane concentration in vessel.	Acid / Butane supply fault.	Less liquid Butane passed to Separator, level and flow control required.

Apparatus: Condenser			
Line Number : Unit			
Intention : Condense Butane vapour by direct contact with cold acid stream.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More / Less	Mixing	Higher / lower supply flows.	More / less intimate contact - condensation more / less likely. If less condensation occurs there is a possibility of vapour build-up: flow, temperature, pressure and level control would be required to compensate.
More	Butane concentration in vessel.	Acid / Butane supply fault.	Incomplete condensation of Butane, build-up of vapour, temperature, pressure and level control required.
Less	Butane concentration in vessel.	Acid / Butane supply fault.	Less liquid Butane passed to Separator, level and flow control required.

Apparatus: Separator			
Line Number : 9			
Intention : Liquid Butane feed from Separator to Flash Unit.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Flow	Feed flow high or level gauge not functioning in Separator.	Too high a feed flow to the flash unit, resulting in temperature and pressure build-up. Pressure controlled also pressure relief valves positioned at relevant points.
More	Pressure	Separator pressure is high - loss of control of upstream compressor.	More Butane vaporised than required, less Liquid Butane feed to Crystalliser. Loss of control at Crystalliser prevented by level and pressure control. Use of diaphragm pumps will give constant feed to Crystalliser from Flash vessel.
Less	Flow	Feed flow low or level gauge not functioning correctly.	Insufficient Butane feed to the Flash vessel. Vapour build-up in Flash vessel - Increasing explosion hazard. Pressure relief operated to reduce pressure, by venting to atmosphere, and increase flow to Flash vessel.

Apparatus: Separator			
Line Number : 10			
Intention : Concentrated acid outlet from separator.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Flow	Level gauge error or pump fault or loss of downstream control.	Possible Butane in outlet - fail-safe level control, where the float will drop but never will show higher than the Acid / Butane interface.
More	Temperature	Loss of control at Condenser	High acid outlet temperature - hazardous fumes requiring downstream action.
Less	Flow	Less feed to the Separator or level	Acid in liquid Butane stream requiring acid resistant pipework, recommended even for the Butane lines because of acid vapour entrainment.

Apparatus: Separator			
Line Number : Unit			
Intention : Facilitate separation of immiscible acid / Butane mixture.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Butane Sensors.	Fault.	Auto-alarm from sensors when failure occurs.
More	Mixing	High turbulence generated by high flowrates. Butane vapour in Separator.	Incomplete separation , Butane vapour in acid outlet - pick-up by Butane sensors, followed by alarm and auto-shutdown. Increased pressure in separator - operation of pressure relief valve.
More	Butane concentration in vessel	High Butane concentration in feed from Condenser.	Action at Condenser.
Less	Mixing	Less turbulence.	Better separation.

Apparatus: Flash - Flash vaporisation of liquid Butane from 4.2 - 0.2 Bar to give required vapour/liquid split.			
Line Number : 11			
Intention : Liquid Butane feed to Flash vessel.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
As for Separator Line 9			

Apparatus: Flash

Line Number : 12

Intention : Butane vapour recycle to Condenser

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Flow	No pressure difference between Condenser and Flash vessels or Compressor failure or Blockage or Leak.	Level gauge control to avoid downstream problems. Butane sensor pick-up and alarm leading to automatic shut-down.
Less	Flow	Pressure in Flash vessel too high or Low feed flows.	Pressure and level control to prevent downstream ramifications.

Apparatus: Flash

Line Number : Unit

Intention : Flash vaporisation of n-Butane at 4.2 bar gauge, to liquid and vapour streams at 0.2 bar gauge.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
More	Vaporised	Pressure difference between feed line and Flash is too high.	Pressure control and pressure relief valves to ensure correct pressure differentials are maintained.

Apparatus: Compressor			
Line Number : Unit			
Intention : Compress Butane vapour stream from 0.2 - 4.2 bar gauge.			
Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Flow	No flow from upstream or Blockage or Leak	Possible evacuation of Flash / Crystalliser units, reliant on level gauge control. Butane sensor alarm and subsequent shutdown.
High	Acid feed concentration	Entrained acid in Butane vapour.	Visible knockout pot will be placed before the compressor to prevent acid attack at the compressor. Compressor diaphragm will be constructed from Neoprene, i.e. acid and Butane resistant.

Apparatus: Level Gauges

Line Number : Unit

Intention : Control / Instrumentation for both liquid Butane and acid in each of the 4 major vessels.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
No	Level control	Mechanical fault -float sinks.	As in the Crystalliser unit HAZOP, if the float sinks the system will fail-safe on low level limit.
		Mechanical fault - float sticks.	The computer still receives signals and, therefore, will assume that the level indicated is the actual level. 1) If the actual level rises in the Crystalliser, the acid enters the Flash raising the level initiating the flash level control, the temperature will increase and the pressure fall in the Crystalliser initiating the control system. 2) If the actual level falls in the Crystalliser, the temperature will fall again setting off the control system. 3) The level cannot rise in the Condenser as the vessel is run at near full liquid loading under normal operating conditions. 4) If the actual level in the Condenser falls there will be less condensation, thus lowering the temperature. There will be less flow to the Separator, initiating the Separator level control.

Continued

Apparatus: Level Gauges

Line Number : Unit

Intention : Control / Instrumentation for both liquid Butane and acid in each of the 4 major vessels.

Guide Word	**Possible Deviation**	**Possible Cause**	**Consequences and Action**
		Mechanical fault -float sticks (continued).	5) The Separator vessel has a level switch as a back-up to its level gauge control, eliminating the hazard. 6) If the actual level in the Flash vessel falls, less Butane will enter the Crystalliser, raising the temperature and, therefore, initiating the control system. 7) If the flash vessel overfills, the Butane will flow back to the Crystalliser unit, setting the Crystalliser unit level control into operation. If adjusting the Butane flow has no effect, then the Flash vessel level gauge is at fault.
No	Common mode level gauge failure.	Electrical / Computer failure.	Fail - Safe emergency shut-down procedure initiated.

APPENDIX 2

Hazard Analysis (HAZAN)

The probability of a hazardous incident occurring can be estimated using a fault chart (Fig. 26) or Logic Tree.

For an "or" junction the probabilities of each branch are added. With an "and" junction the probabilities are multiplied together. An estimate of the total probability of a hazardous situation occurring can then be made. In the case of the S.O.R.C., actual data on probability of failure are not available, therefore, estimates have been made which are not accurate but which give a guide to the magnitude of the likelihood of failure.

Probability of level gauge failure, resulting in a hazardous situation, is estimated at 0.5 failures per year of operation, i.e. 1 failure every 2 years.

Probability of sensor, pressure or temperature, failure is estimated at 1 failure per year.

Probability of compressor/pump failure is estimated at 1 failure per year.

Probability of pipe/vessel fracture is estimated at 0.01 failures per year.

Probability of sensor or gauge error resulting in a hazardous situation, is estimated at 1 failure per year.

Probability of Oxygen building up in the system to a dangerous level is estimated at 0.01 times per year.

Probability of loss of computer control or a failure of the power supply is estimated at 0.1 failures per year.

Probability of the Butane sensors failing is estimated at 0.1 failures per year.

Probability of an ignition source occurring in an intrinsically safe zone was estimated at 0.1 times per year.

Using the fault chart, Figure 26, the probability of an incident occurring that results in catastrophic failure and hazard to life is low at 0.02625, i.e. an incident occurring once every 38 years.

This would not be satisfactory for a production plant, but following discussions with the Health and Safety Executive and British Steel safety representatives, this was considered satisfactory for the pilot plant experimentation, considering the constraints imposed on access to the test facility and the duration of the proposed test programme

APPENDIX 3

Dow Fire and Explosion Indices.

The Index is calculated as below and using Figures 28-31.

Index Range:

0-20	Mild
20-40	Light
40-60	Moderate
60-95	Heavy
>95	Extreme

The dominant material is n-Butane, both in its liquid and vapour states.

Material factor = $(-H_c * 0.00043)/Mw$

where H_c = standard heat of combustion =-2655KJ/mol.

Mw = molecular weight = 58

Material factor for n-Butane = 2655000*0.00043/58 = 19.7

The special material hazards, general process hazards and special process hazards applicable to each major unit in the S.O.R.C. pilot plant can be found in Figure 27.

These were combined, as in Figure 28, to give an index of 115.9 for the Crystalliser, which is in the **Extreme** range.

In Figure 29, an index of 93.1, in the **Heavy** range, was calculated for the Condenser.

In Figure 30, an index of 37.3, in the **Light** range, was calculated for the Separator.

In Figure 31, an index of 121.2, in the **Extreme** range, was calculated for the Flash vaporisation unit.

APPENDIX 4.

Method for Gas Chromatographic Determination of Butane Contamination of Crystals.

Approximately 1 gm. of crystals were accurately weighed and placed in a small sample tube and sealed with a Suba seal septum. The tube was heated for 2-3 minutes on the edge of a hot plate at 100 °C.

A 25 µl aliquot was taken from the tube via the septum using a gas tight syringe and injected into the column using conditions outlined below:

Chromatograph - Pye Unicam PU4500

Column - 1525 mm Copper column containing 10% Se30 on Chromosorb G.

Column Temperature - 50°C.

Detector - Flame ionisation.

Detector Temperature - 200°C.

Carrier Gas - High purity Nitrogen.

Carrier Gas Flow - 40 ml/min.

Attenuation - 200

The peak areas obtained for the samples were compared to a calibration graph prepared from standard injections of n-Butane gas determined under identical conditions. To ensure that all the n-Butane had been accounted for, the tubes were reheated until a constant peak area was obtained for n-Butane. It was found, however, that 2-3 minutes was sufficient to release any n-Butane in the crystals.

The standard method of reporting is to give the contamination as μl/g of sample, a simple calculation results in a conversion factor of $2.5*10^{-4}$ to give the contamination as % by weight.

	Tank No. 1	Tank No. 2	Tank No. 3	Tank No. 4	Tank No. 5
Sulphuric Acid wt %	8	12	18	23	25
Iron (2) Sulphate wt %	18	17	12	5	4

TABLE 1 : TYPICAL CONTINUOUS PICKLE LINE ANALYSES

Refrigerant	Pressure (Bar absolute) at Temperature T					
	-10°C	0°C	10°C	20°C	30°C	40°C
N-Butane	0.707	1.042	1.492	2.083	2.842	3.798
Propane	3.461	4.762	6.462	8.429	10.894	13.844
Carbon Dioxide	26.714	35.186	45.441	57.667	72.962	-
Trichlorofluoro Methane (Refrigerant 11)	0.262	0.408	0.615	0.897	1.273	1.762
Dichlorodifluoro Methane (Refrigerant 12)	1.953	3.129	4.301	5.755	7.593	9.794
Dichlorofluoro Methane (Refrigerant 21)	0.465	0.718	1.071	1.547	2.174	2.981
Chlorodifluoro Methane (Refrigerant 22)	3.616	5.075	6.936	9.259	12.102	15.522

TABLE 2 : PRESSURE / TEMPERATURE RELATIONSHIPS FOR SOME COMMON REFRIGERANTS

	Scan No.	Oxygen level Volume %
Test 1	215	1.1
	220	0.4
	225	0.3
	425	2.2
	430	1.3
	435	0.4
	500	2.3
	505	1.5
	510	0.4
Test 2	100	2.0
	180	0.1
	266	0.1
	550	0.2

N.B. During test 2, the condenser vent valve was opened for 5 seconds prior to taking the samples.

TABLE 3 : OXYGEN ANALYSIS AT THE TOP OF THE CONDENSER VESSEL

Sample	Solution analysis wt % Sulphate.	Temperature of sample. °C	Crystal contamination by n-Butane µl/g (wt %)	Comment
1	68.3	-	-	As supplied
2	46.4	11	-	
3	33.3	6	2.6 (683*10^{-6})	
4	43.9	10	-	
5	40.9	8	1.1 (285*10^{-6})	
6	39.8	9	1.8 (568*10^{-6})	
7	38.1	10	2.4 (624*10^{-6})	Held for 30 minutes in crystalliser.
8	38.6	-	-	Sample at exit of Separator.

TABLE 4 : ANALYSIS OF IRON (2) SULPHATE IN AQUEOUS SOLUTION AND CRYSTALS PRODUCED DURING THE SEMI-OPEN REFRIGERATION CYCLE.

Sample No.	**Solution analysis wt % Sulphate**	**Temperature of sample. ^{o}C**	**Crystal contamination by n-Butane μl/g (wt %)**	**Comment**
1	45.7	-	-	As supplied
2	38.7	14.9	-	
3	29.4	10	-	
4	29.4	6.8	0.2 ($52*10^{-6}$)	
5	28.7	6.4	0.1 ($26*10^{-6}$)	
6	27.5	6	0.1 ($26*10^{-6}$)	
7	28.3	6.6	1.7 ($440*10^{-6}$)	Sample wet.

TABLE 5 : ANALYSIS OF COPPER (2) SULPHATE SOLUTIONS AND CRYSTALS

Sample No.	**Solution analysis wt % Iron (2) Sulphate**	**Solution analysis wt % Sulphuric Acid**	**Temperature of sample. °C**	**Crystal contamination by n-Butane. µl/g (wt %)**	**Comment**
1	27.7	20.2	-	-	As supplied
2	27.7	18.9	6	1.7 ($440*10^{-6}$)	Slow cooling
3	23.4	19.5	11	1.1 ($285*10^{-6}$)	
4	21.5	20.9	7.5	0.2 ($52*10^{-6}$)	
5	22.6	20.3	4.5	0.1 ($26*10^{-6}$)	
6	13.8	20.2	~6	0.4 ($104*10^{-6}$)	Temperature held for 30 minutes

TABLE 6 : ANALYSIS OF IRON (2) SULPHATE IN TREATED WASTE PICKLE LIQUOR AND CRYSTALS PRODUCED DURING THE SEMI-OPEN REFRIGERATION CYCLE

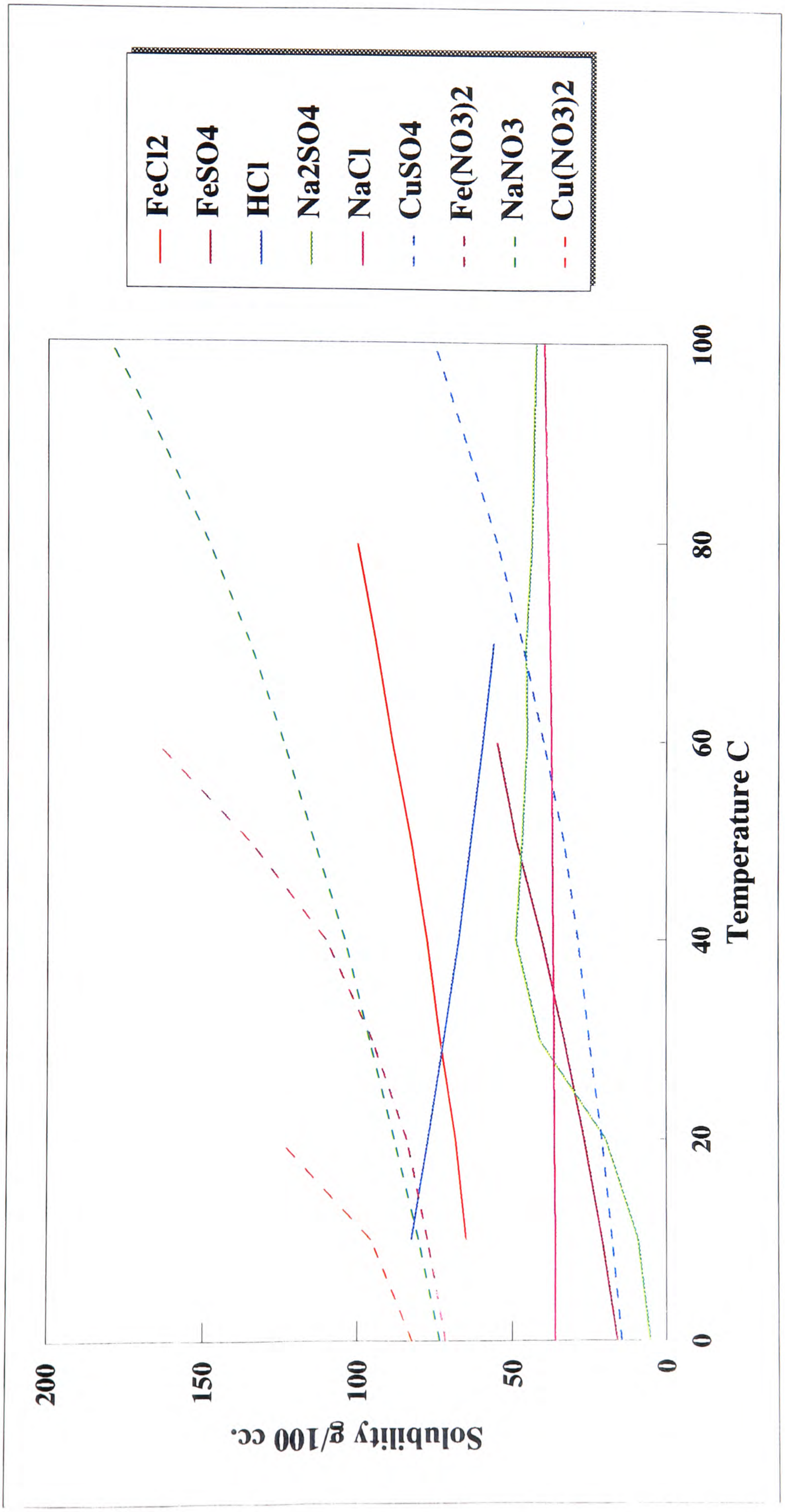


Fig. 1 Solubility of Some Common Inorganic Salts

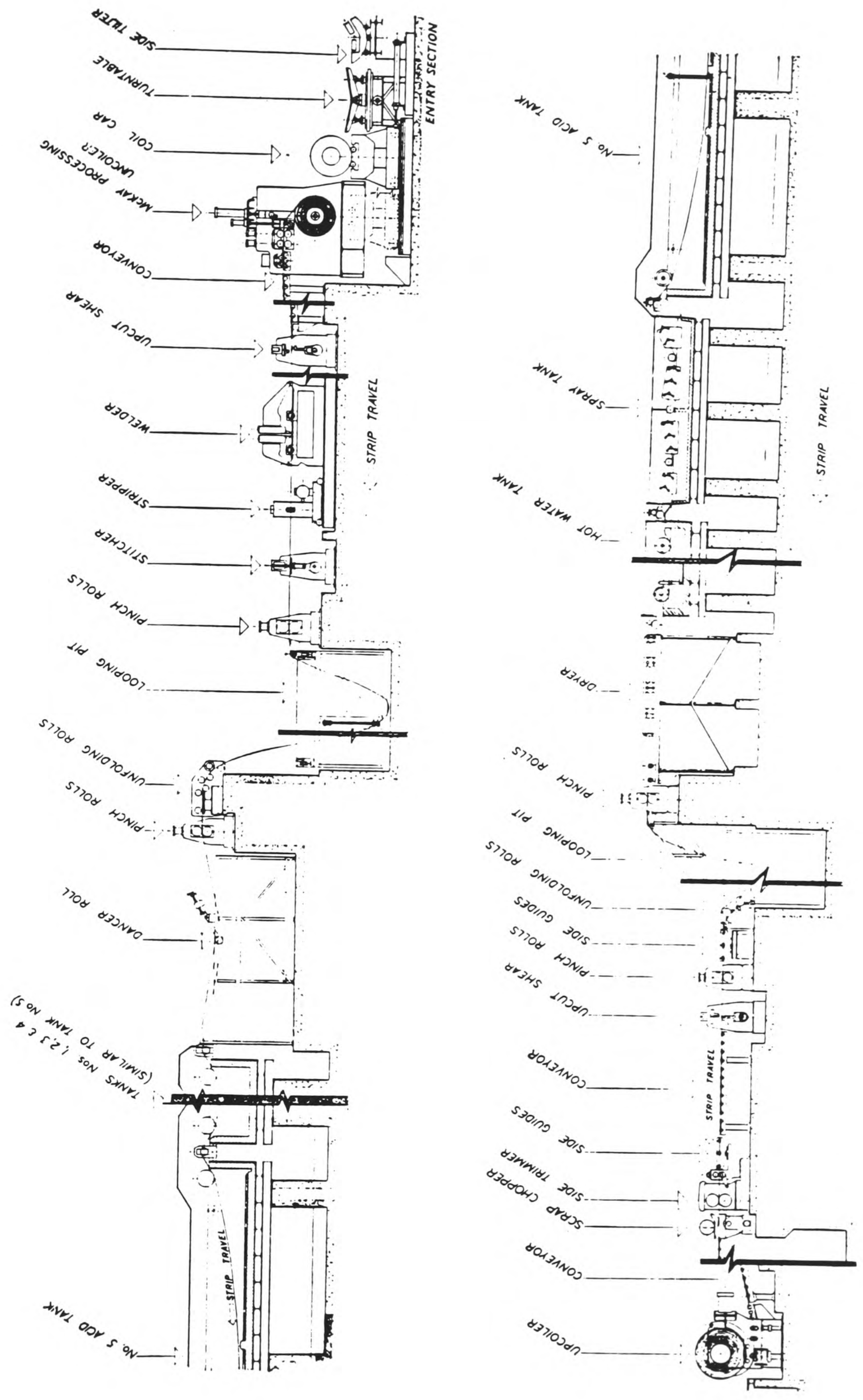


Fig. 2 Schematic Arrangement of a Typical Continuous Pickling Line

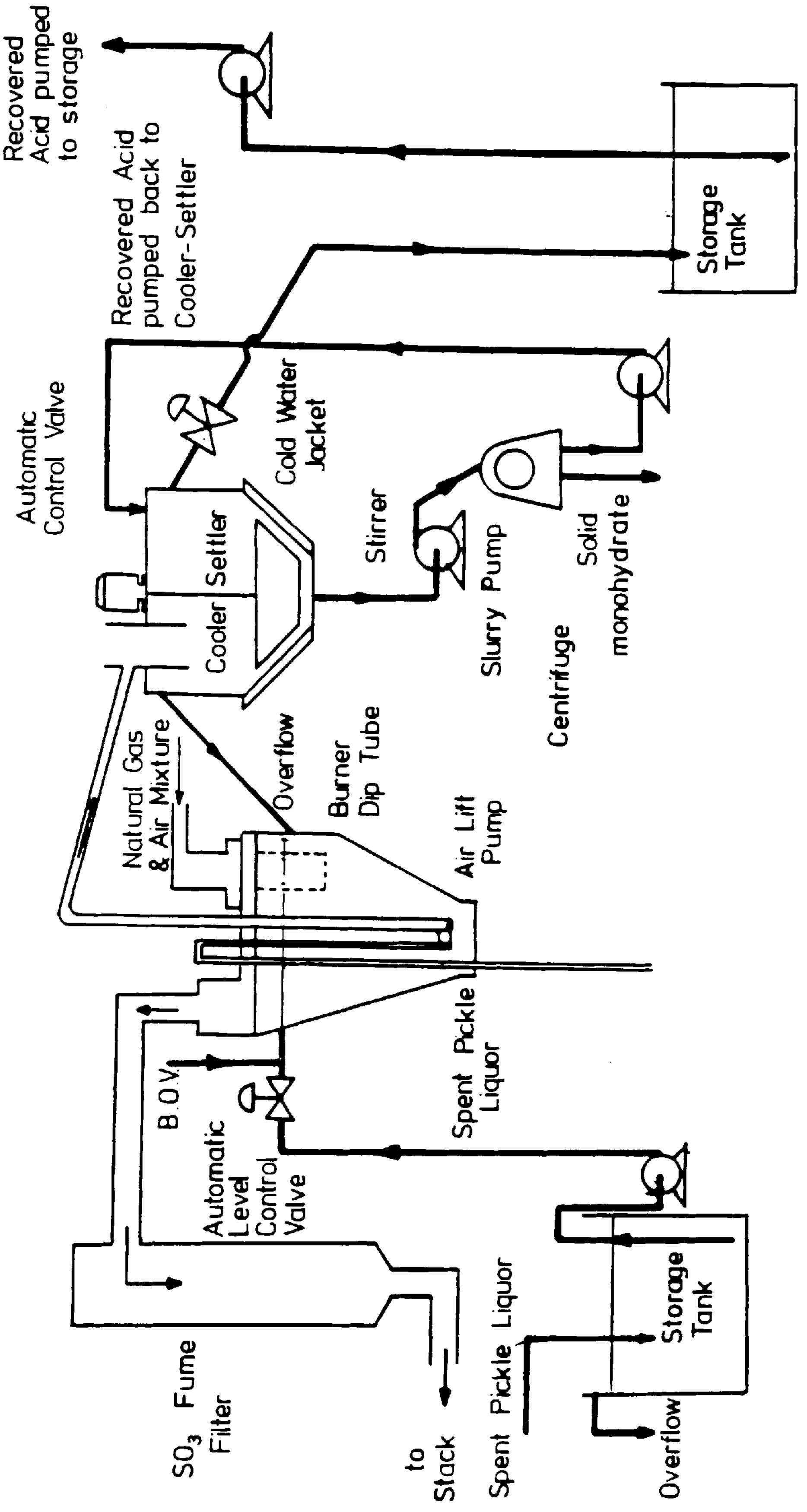


Fig. 3 Nordac System for Sulphuric Acid Recovery

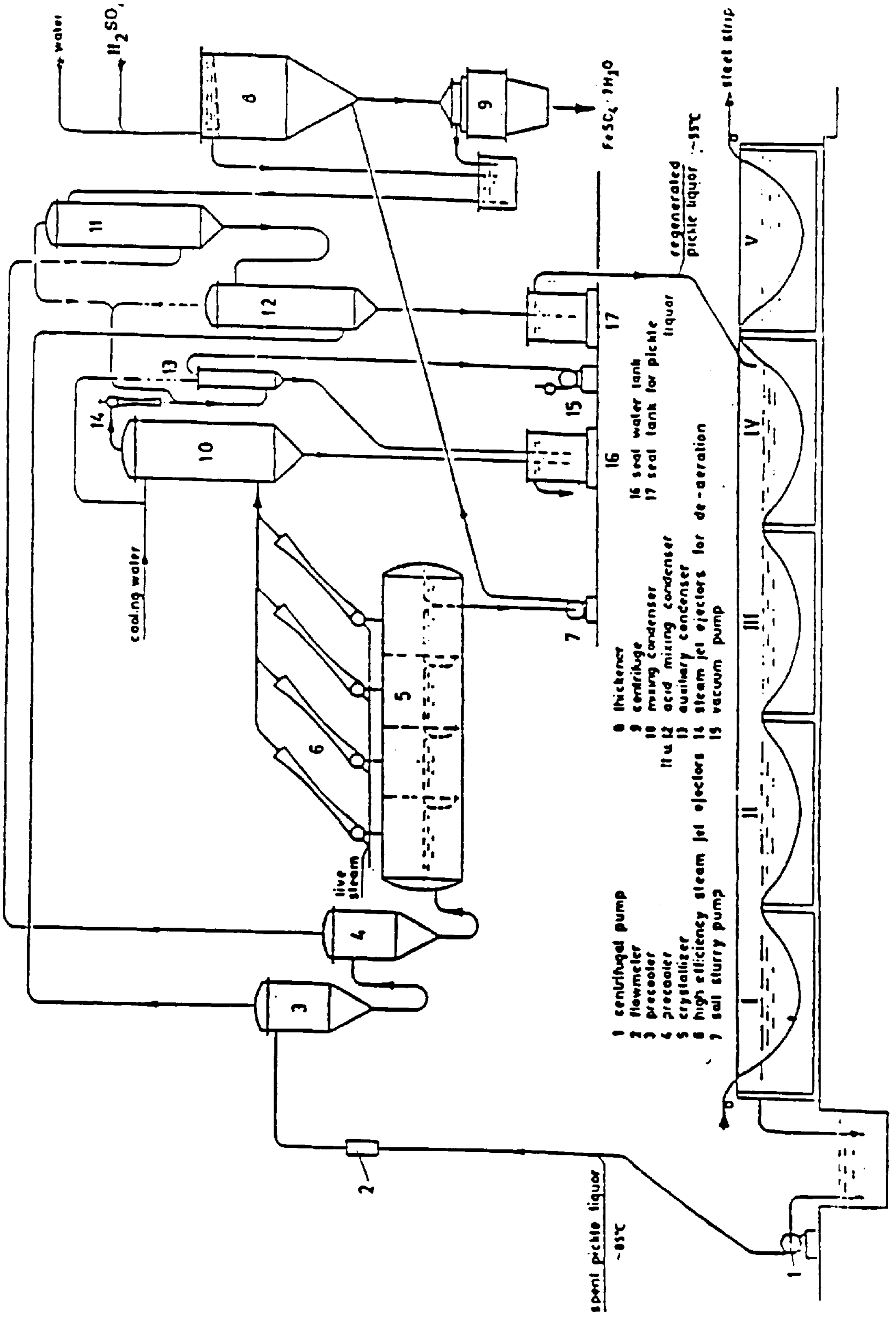


Fig. 4 General Arrangement of Pickle Line / Vacuum Recovery Plant

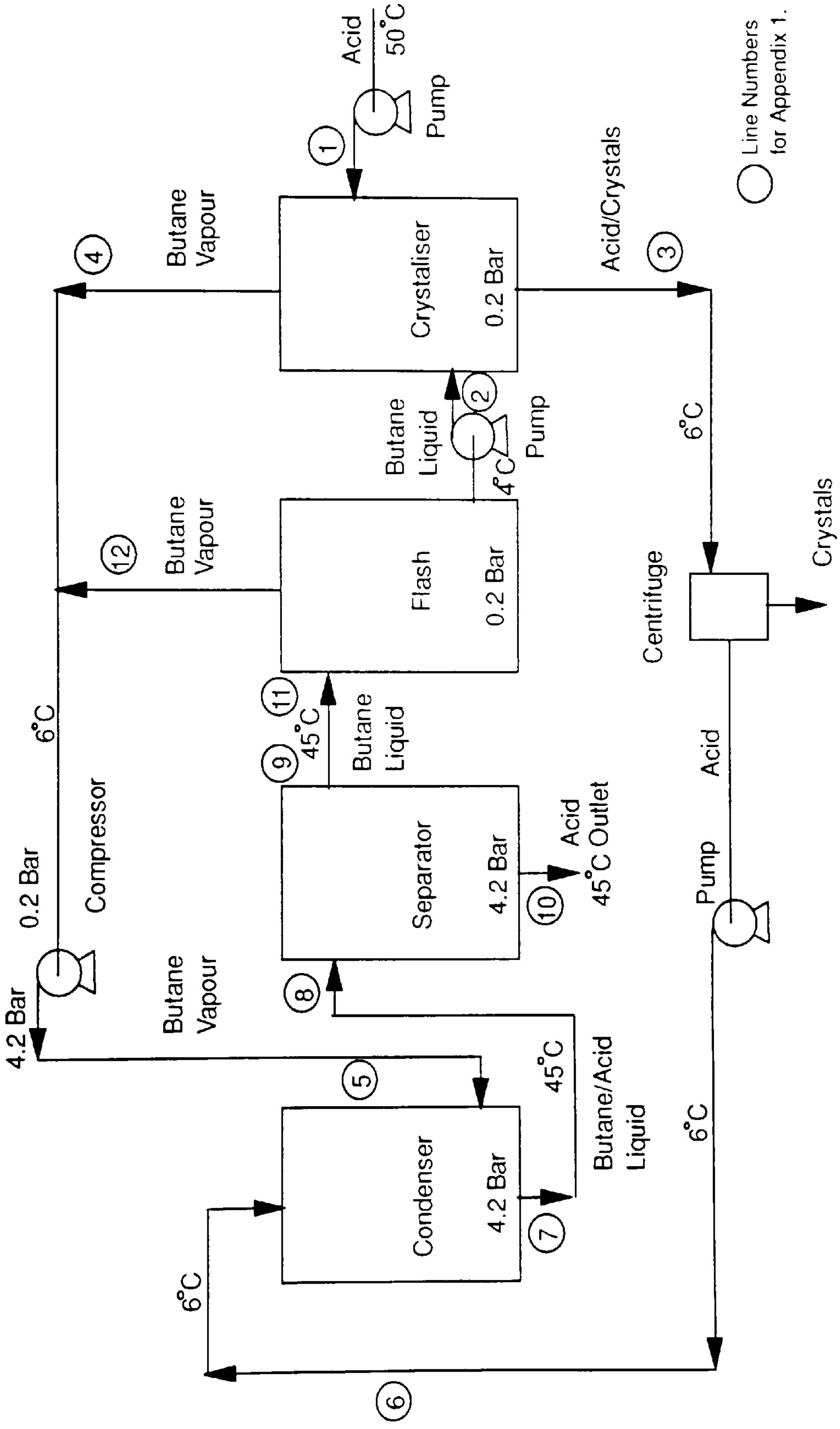
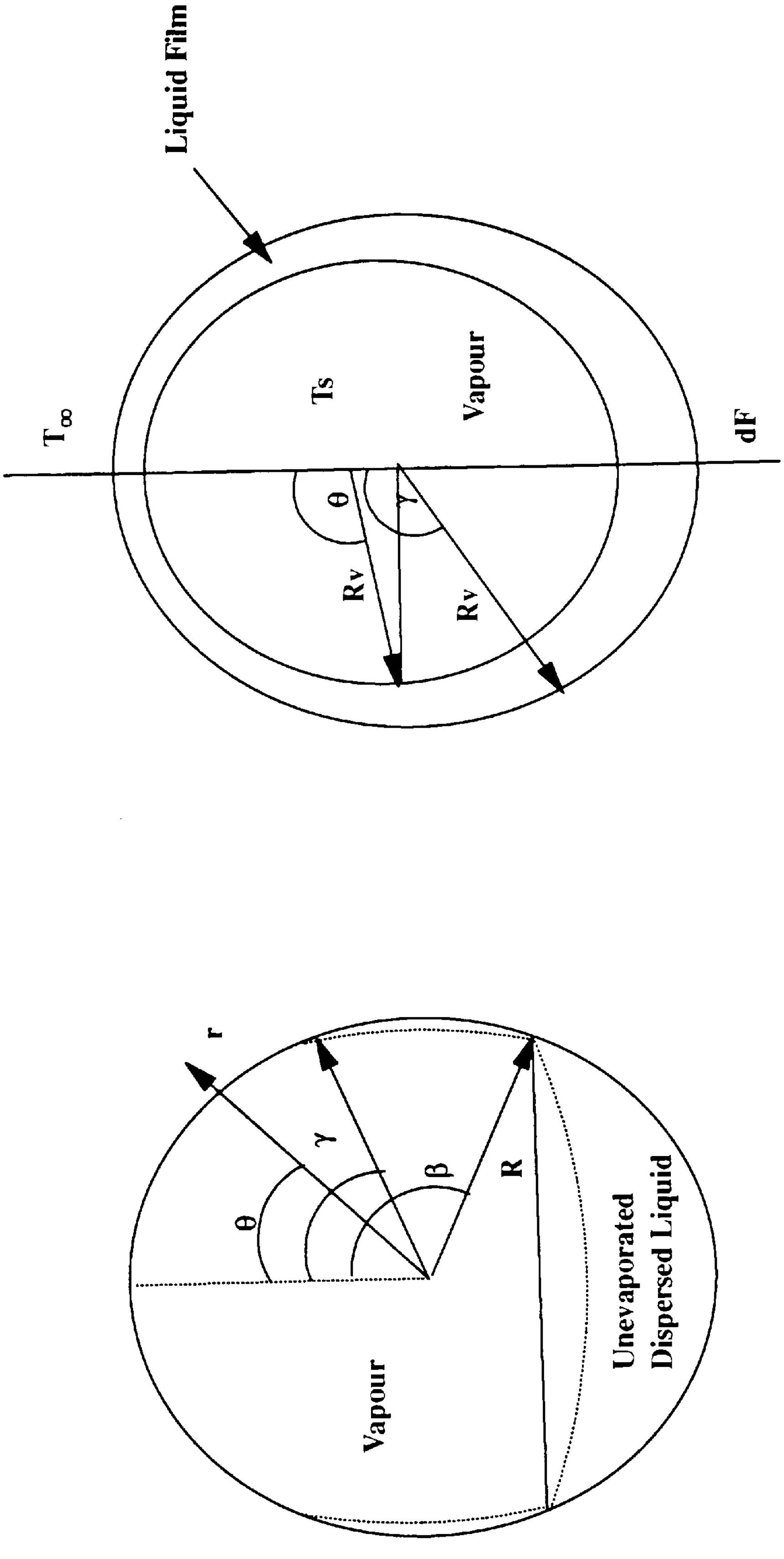


Fig. 5 Semi-Open Refrigeration Cycle



Condensation : as described by Kalman and Letan

Evaporation : as described by Raina and Wanchoo

Fig. 6 Evaporation and Condensation of a Bubble

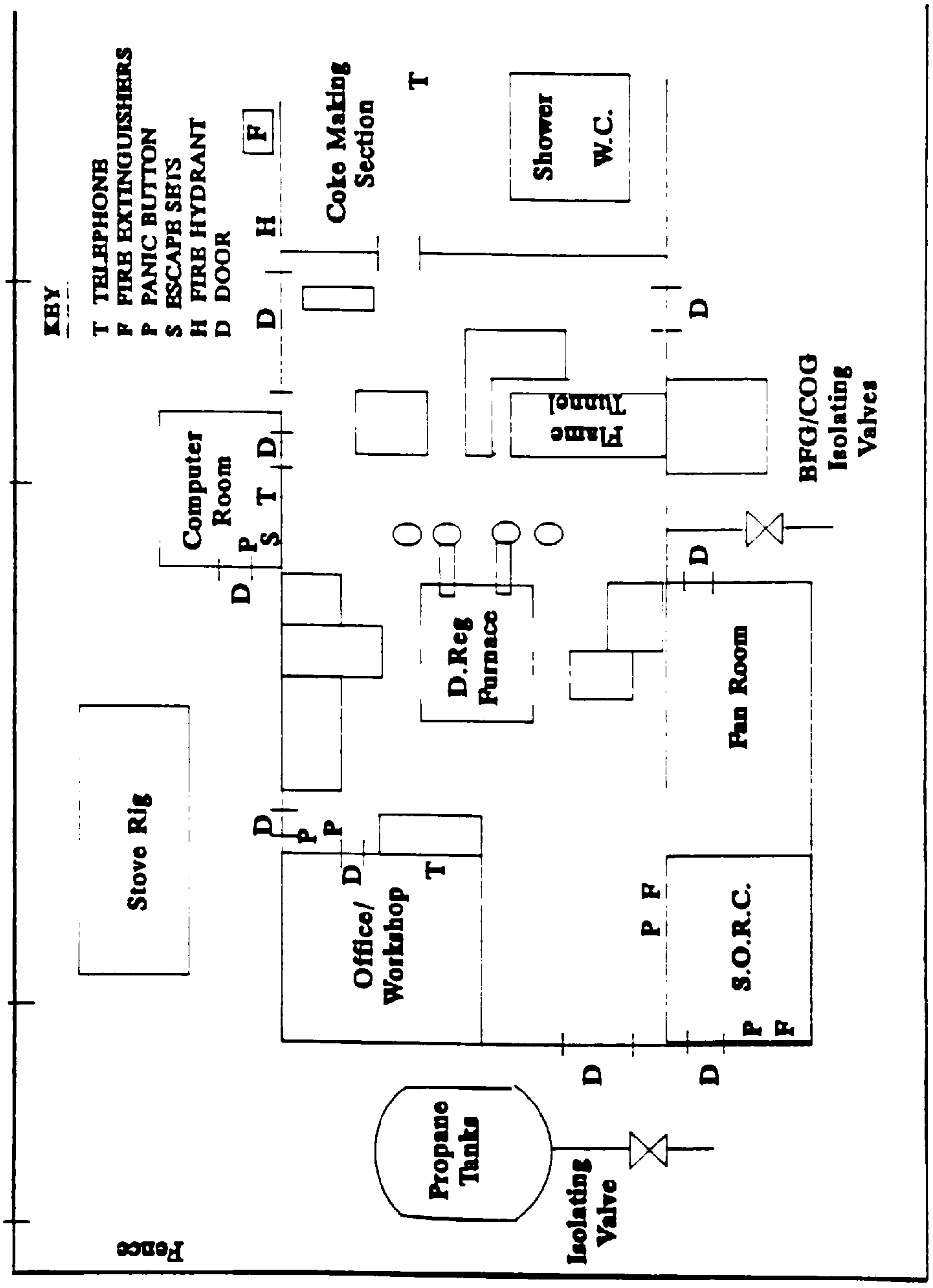


Fig. 7 General Arrangement of Energy Research Test Facility

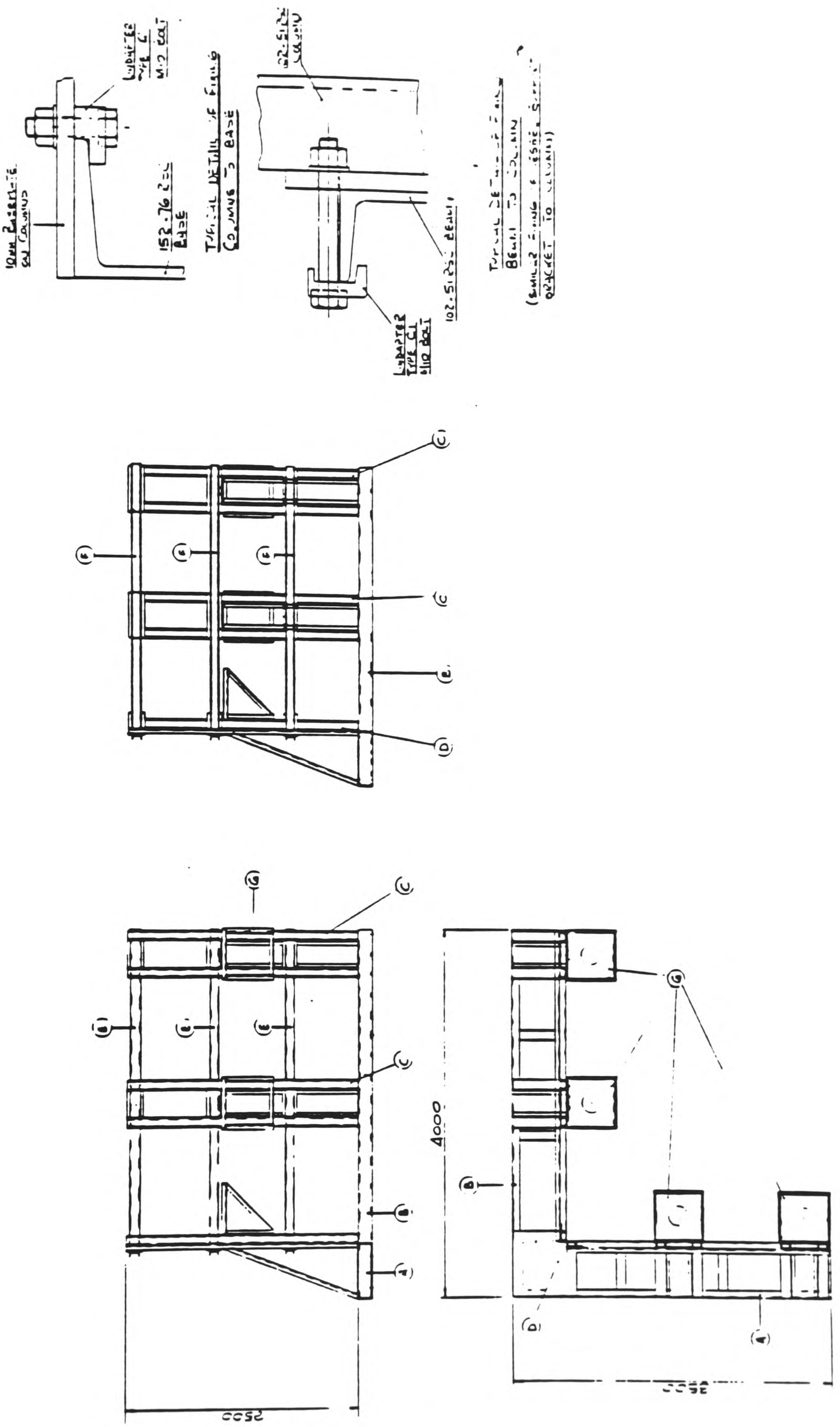


Fig. 8 Supporting Framework for Pilot Plant

ORIGINATING OFFICE DRG. No.

RECEIVING OFFICE DRG. No.

FIRST ANGLE PROJECTION

CONFIDENTIAL – BRITISH STEEL CORPORATION

DO NOT SCALE

VALVE AND FITTINGS SCHEDULE

QTY	ITEM	DRG OR MAT'L	DESCRIPTION
2	1	NUPRO-4CPA SERIES	1/4" FEMALE NPT ADJUSTABLE RELIEF VALVE~SS-4CPA2-3
2	2	WHITEY-F10E SERIES	3/4" NPT BALL VALVE ~ SS-F65TF12
31	3	" "	1/2" NPT " " ~ SS-F63TF8
4	4	SWAGELOK	1/4"-1/8" REDUCER ~ SS-200-R-4
6	5	NUPRO-RL3 SERIES	1/4"-SWAGELOK RELIEF VALVE ~ SS-RL3S4
26	6	SWAGELOK	1/2 NPT MALE CONNECTOR ~ SS-400-1-8
1	7	WHITEY-FORGE BODY	1/4"-SWAGELOK ~ FORGE BODY REG V/V ~ SS-1-RS4
2	8	NUPRO-'B' SERIES	1/4"-SWAGELOK ~ 'B' SERIES AIR ACT BELLOWS ~ SS-4BK-1C (NORMALLY CLOSED)
2	9	PLATON FLOWBITS	AIR OPERATED DIAPHRAGM PUMP ~ TYPE ADP
1	10	RADIO SPARES	LIQUID FLOW SENSOR ~ STOCK No: 630-746
	11	KNF	COMPRESSOR ~ MODEL: N1400 2 ANE
1	12	1506	PRESSURE VESSEL ~ CRYSTALIZER
1	13	1509	" " ~ FLASH
1	14	1507	" " ~ SEPARATOR
	15	1508	" " ~ CONDENSER
5	16	WHITEY	BALL VALVE AIR ACTUATORS ~ MS-133DA
5	17	"	VALVE MOUNTING KIT ~ MS-MB-63
2	18	SWAGELOK	1/4" NPT FEMALE CONNECTIONS ~ SS-810-7-4
2	19	NUPRO-4CPA SERIES	1/4" NPT ADJUSTABLE RELIEF V/V ~ SS-4CPA2-50
6	20	SWAGELOK	3/4" NPT MALE CONNECTORS ~ SS-1210-1-12
33	21	"	1/2" NPT " " ~ SS-810-1-8
25	22	"	1/4" NPT " " ~ SS-400-1-4
1	23		BUTANE PUMP
2	24	SWAGELOK	1/2" NPT FEMALE BRANCH TEE ~ SS-810-3-8TTF
4	25	"	1/2" NPT MALE CONNECTOR ~ SS-400-1-8
3	26	"	1/4"- UNION TEE " ~ SS-400-3
3	27	"	1/2"- UNION TEE ~ SS-810-3
2	28	"	3/4"- FEMALE BRANCH TEE ~ SS-1210-3TTF
2	29	"	3/4" NPT MALE CONNECTOR ~ SS-810-1-12
2	30	"	3/4"- UNION TEE ~ S-1210-3
2	31	"	3/4"-1/2" REDUCER ~ SS-810-R-12
1	32	"	1/2"- FEMALE RUN TEE-SS-810-3-8TFT
	33	"	1/2" NPT MALE CONNECTOR ~ SS-400-1-8
1	34	"	3/4"-1/2" REDUCING UNION ~ S-1210-6-8
1	35	"	1/8"- UNION TEE ~ SS-200-3
2	36	"	1/8" NPT MALE CONNECTOR ~ SS-200-1-2
3	37	"	1/8- UNION ELBOW ~ SS-200-9
22	38	"	1/4" " " ~ SS-400-9
1	39	"	1/2"-1/8" REDUCER ~ SS-810-6-2
2	40	"	1/2"-1/4" " ~ SS-400-R-8
7	41	"	1/2"- UNION ELBOW ~ SS-810-9
5	42	"	3/4"- " " ~ SS-1210-9
	43	ST. STL 316	1/8" O/DIA TUBE × 6M LG (ASTM-A269) .035 WALL
	44	" "	1/4" O/DIA TUBE × 6M LG " " 0.035 WALL THK
	45	CARBON STL	1/4" O/DIA TUBE × 6M LG (ASTM-A179) 0.035 WALL THK
	46	KNF	ADAPTER FITTINGS TO SUIT 3/4" O/D ST. STL 316 TUBE

QTY	ITEM	DRG OR MAT'L	DESCRIPTION
	47	ST STL 316 L	1/2" O/DIA TUBE × 6M LG (ASTM-A269) 0.035 WALL THK
	48	CARBON STL	1/2" O/DIA TUBE × 6M LG (ASTM-A179) 0.035 WALL THK
	49	ST STL 316 L	3/4" O/DIA TUBE × 6M LG (ASTM-A269) 0.065 WALL THK
	50	CARBON STL	3/4" O/DIA TUBE × 6M LG (ASTM-A179) 0.065" WALL
	51	" "	1" O/DIA TUBE × 6M LG " " 0.065" WALL
	52	KNF	ADAPTER FITTING TO SUIT 1/2" O/D STL. STL TUBE 316 L
1	53	SWAGELOK	1/2"-1/4" REDUCING UNION ~ SS-810-6-4
1	54	"	1"-3/4" " " ~ S-1610-6-12

NOTE!
THIS DRAWING TO BE READ IN CONJUNCTION WITH DRG No ~ 1505

No. OFF	ITEM	DRG No OR MATL.	DESCRIPTION

SCALE —
UNIT OF MEASUREMENT —
DRAWN DME 3-6-88
CHECKED
TRACED
PASSED

PLANT PILOT PLANT
SECTION ENERGY
DESCRIPTION VALVE SCHEDULE ~ ACID RECOVERY PILOT PLANT

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ORIGINATING OFFICE WELSH LABORATORY
DRG. No. 1513 – 'A'

RECEIVING OFFICE
DRG. No.

DIVISION CORPORATE RESEARCH ORGANISATN

WORKS WELSH LABS, PORT TALBOT

British Steel Corporation

REVISIONS
A
ITEM 5 WAS 15 OFF. ITEM 53 & 54 ADDED. VARIOUS VALVES DELETED. FITTINGS ADDED. VARIOUS QTYS ALTERED

CONFIDENTIAL
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Fig. 9b Valve Schedule for SORC Pilot Plant

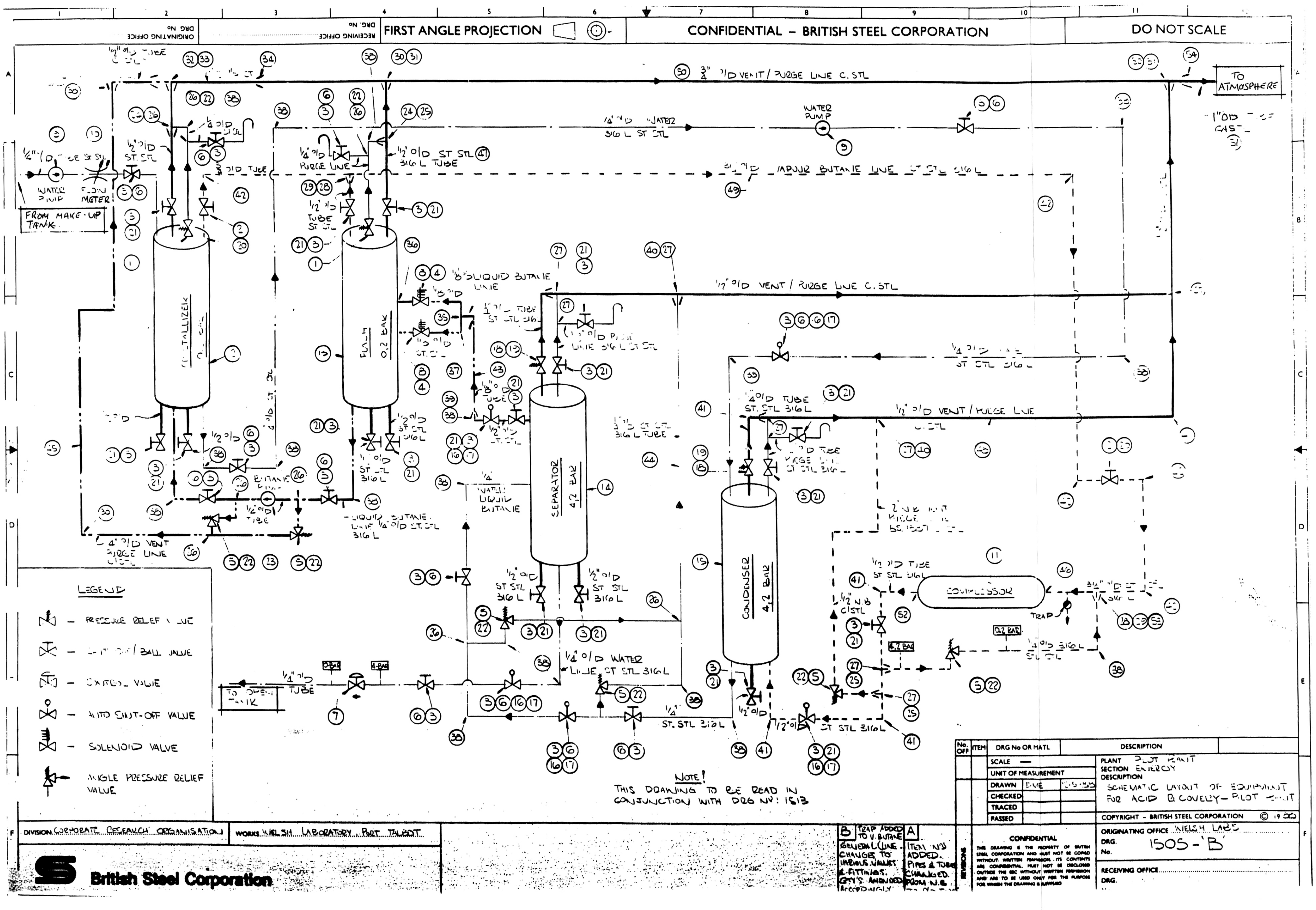


Fig. 9a Schematic Arrangement of SORC Pilot Plant

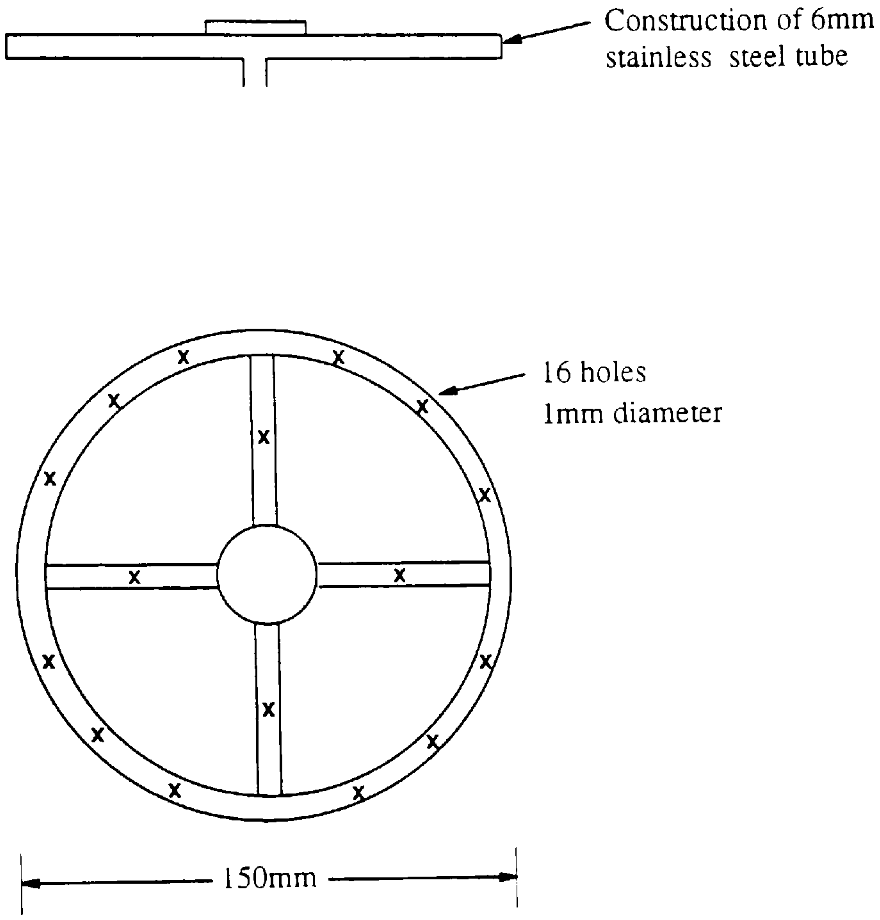


Fig. 10 Crystalliser Nozzle Arrangement

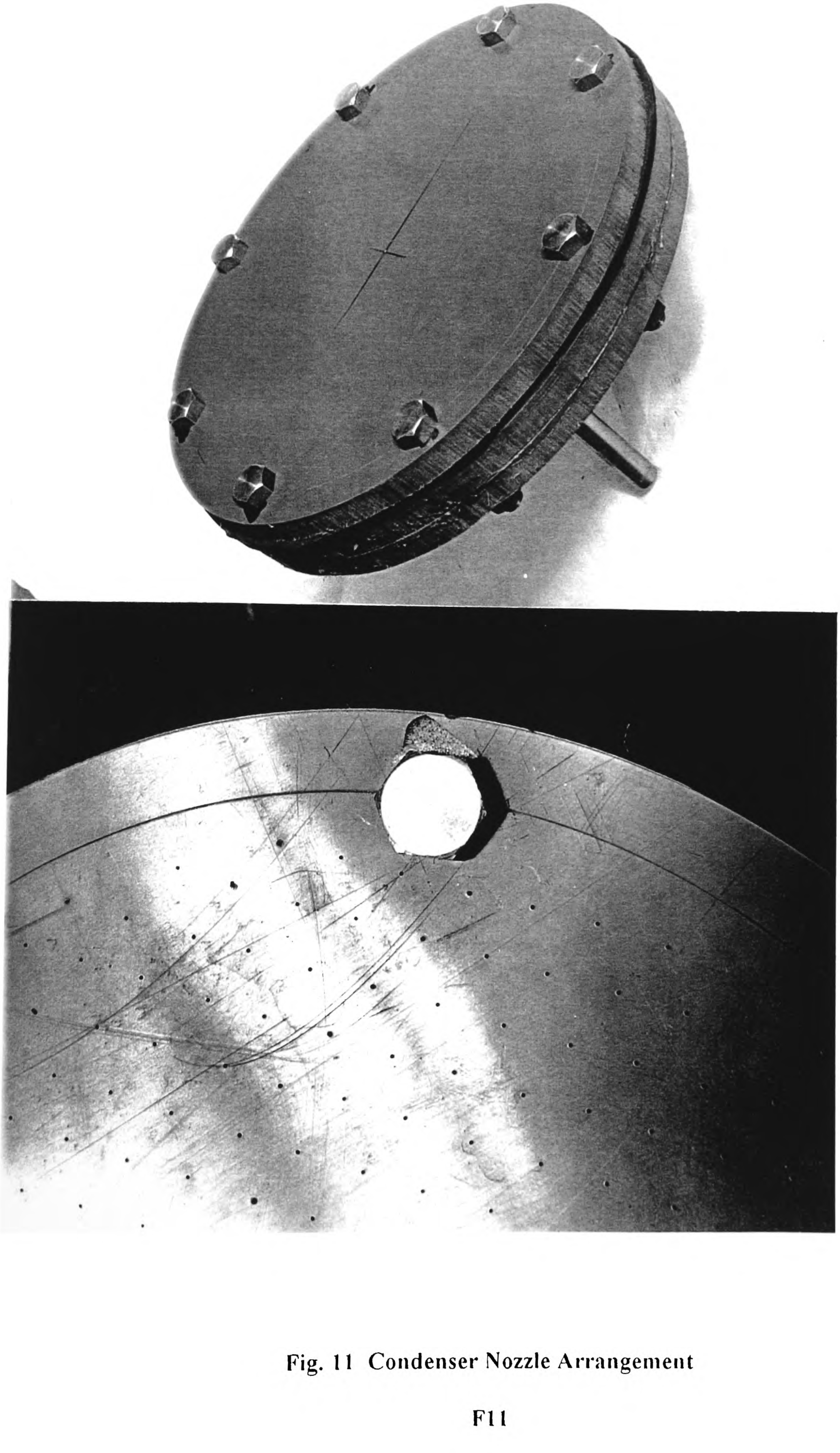


Fig. 11 Condenser Nozzle Arrangement

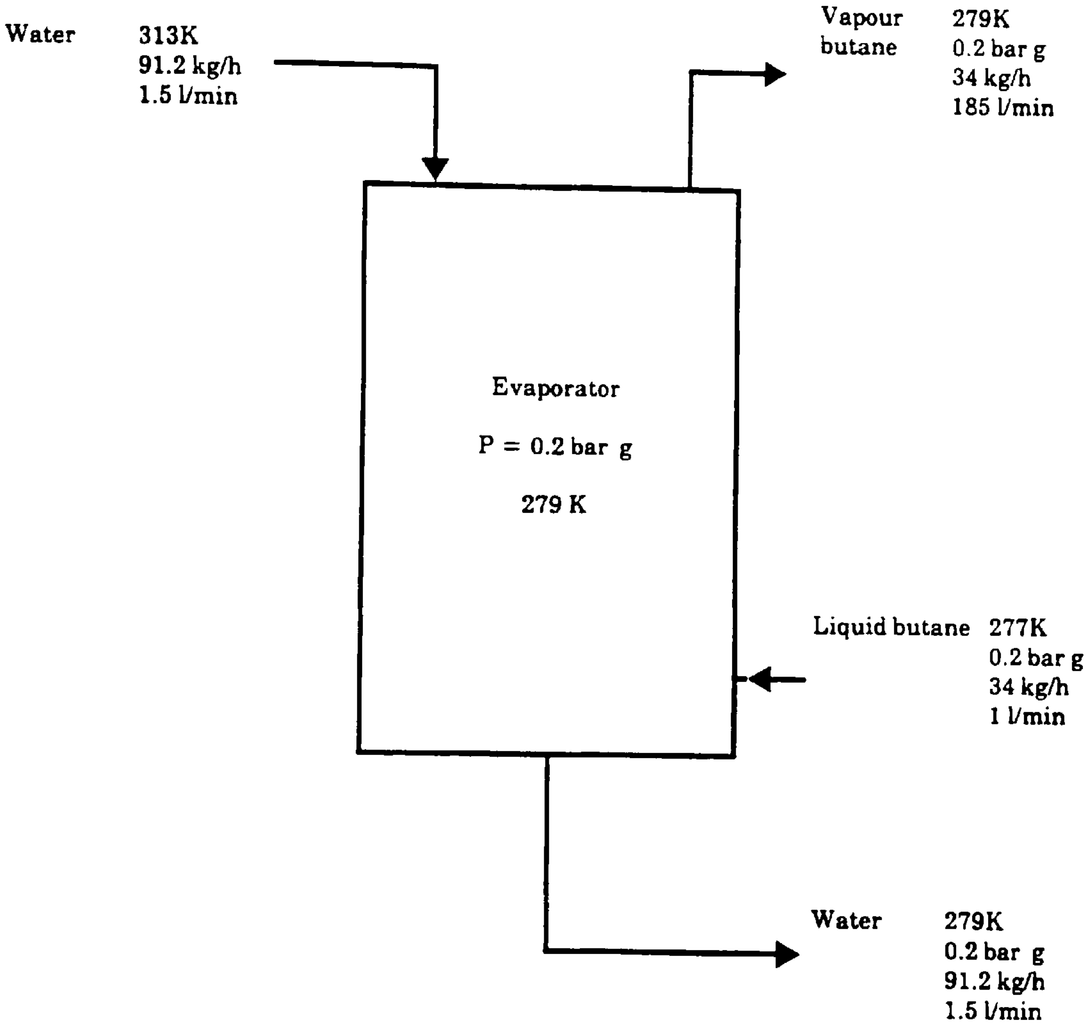


Fig. 12 Mass Flowrates and Conditions around Crystalliser Vessel

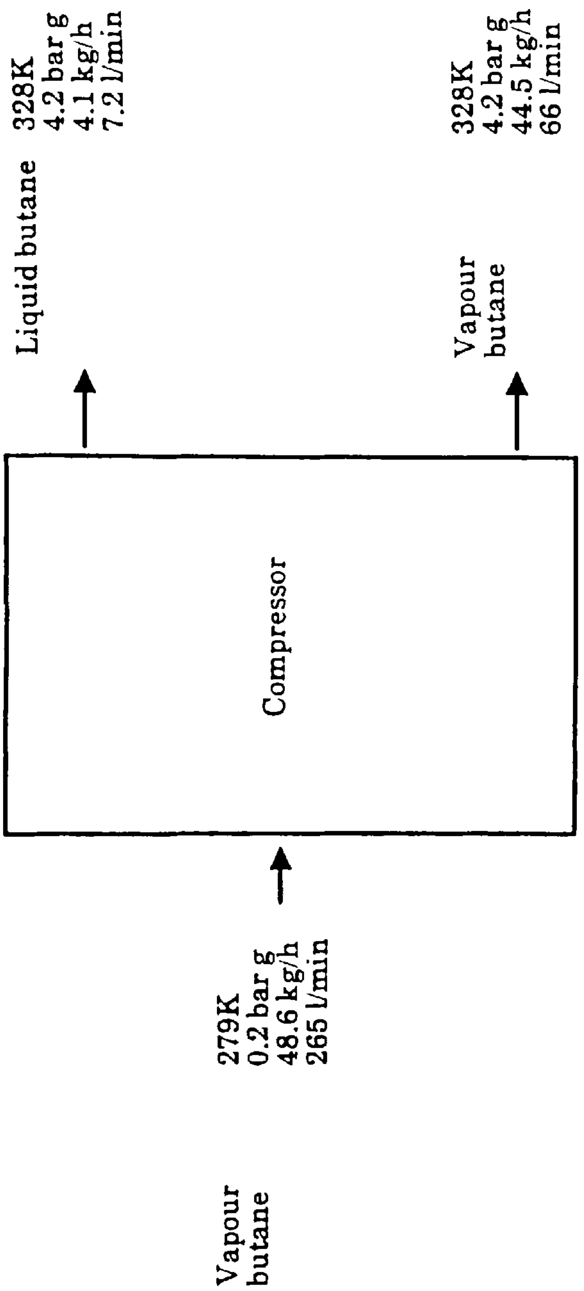


Fig. 13 Mass Flowrates and Conditions around Compressor

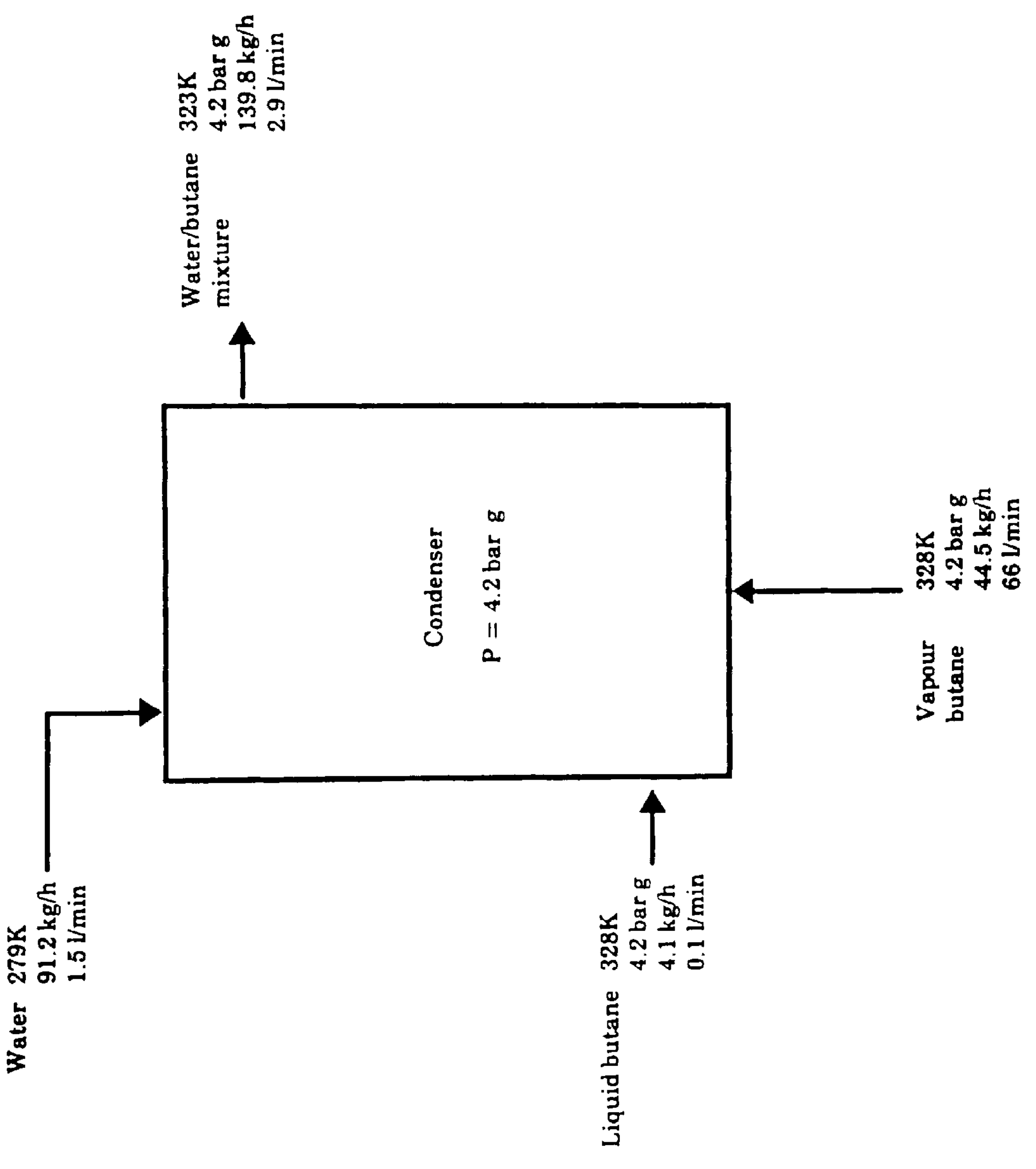


Fig. 14 Mass Flowrates and Conditions around Condenser Vessel

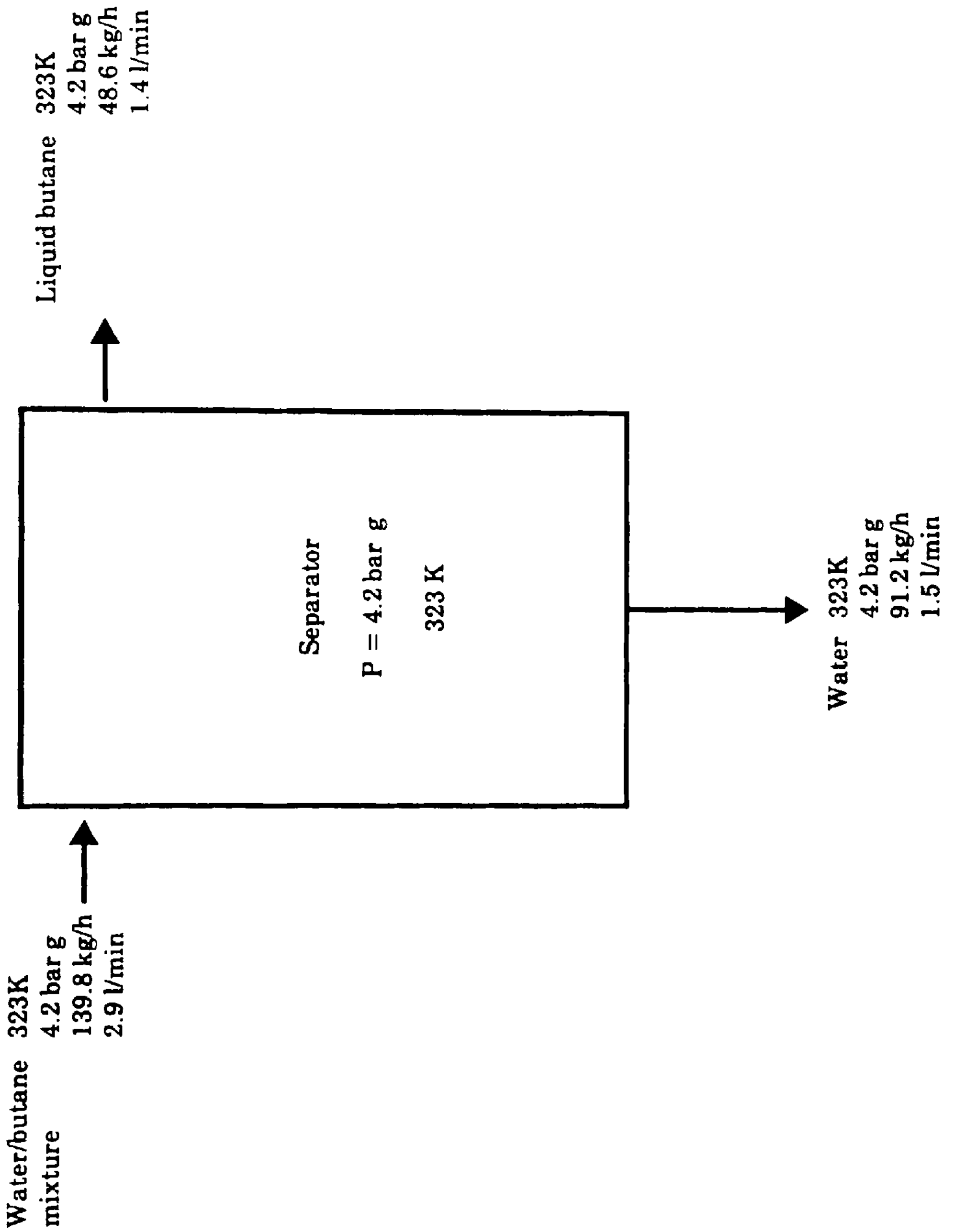


Fig. 15 Mass Flowrates and Conditions around Separator Vessel

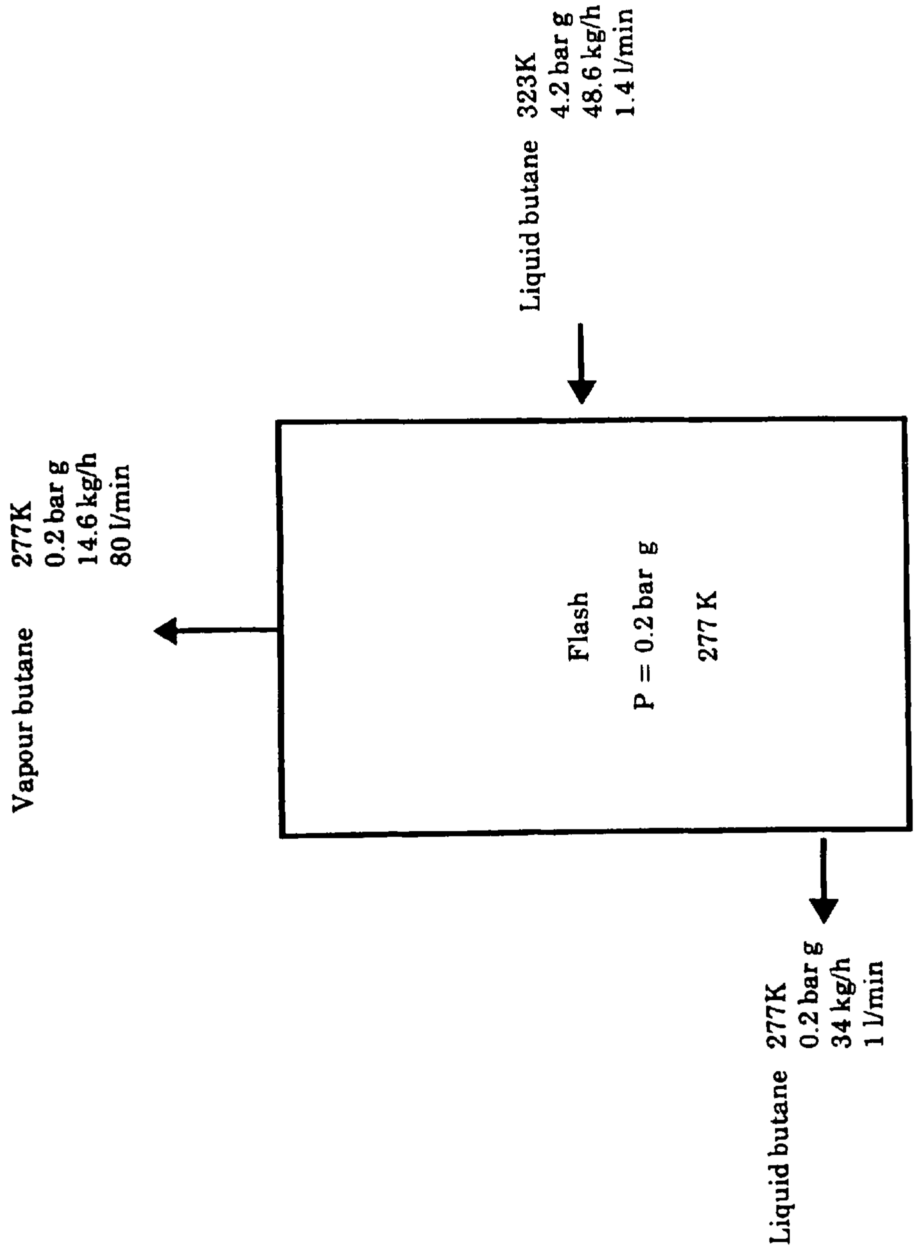


Fig. 16 Mass Flowrates and Conditions around Flash Vessel

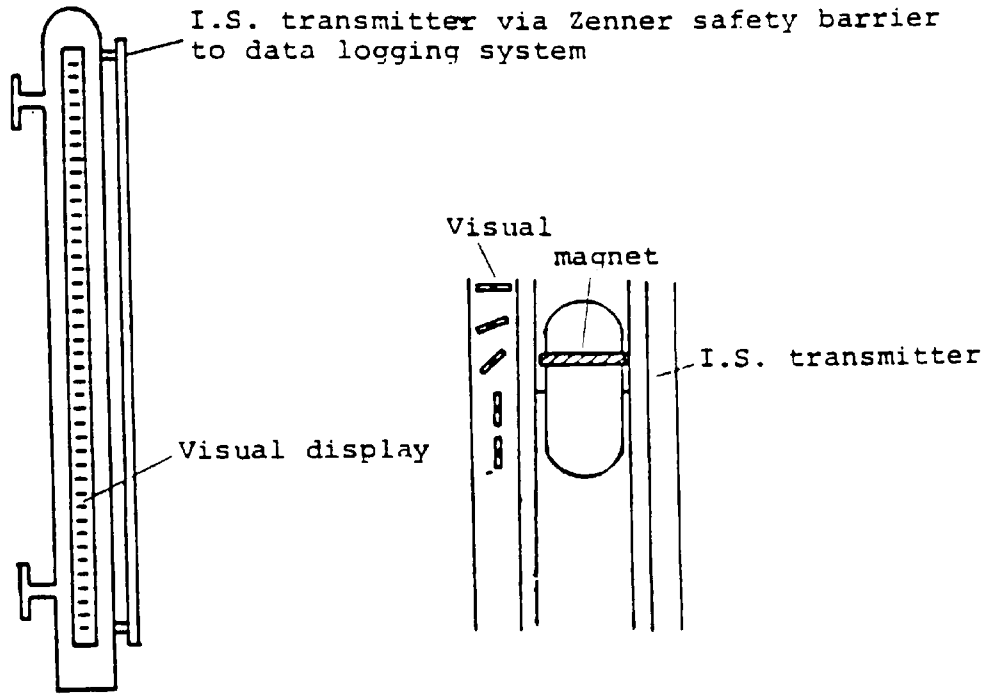
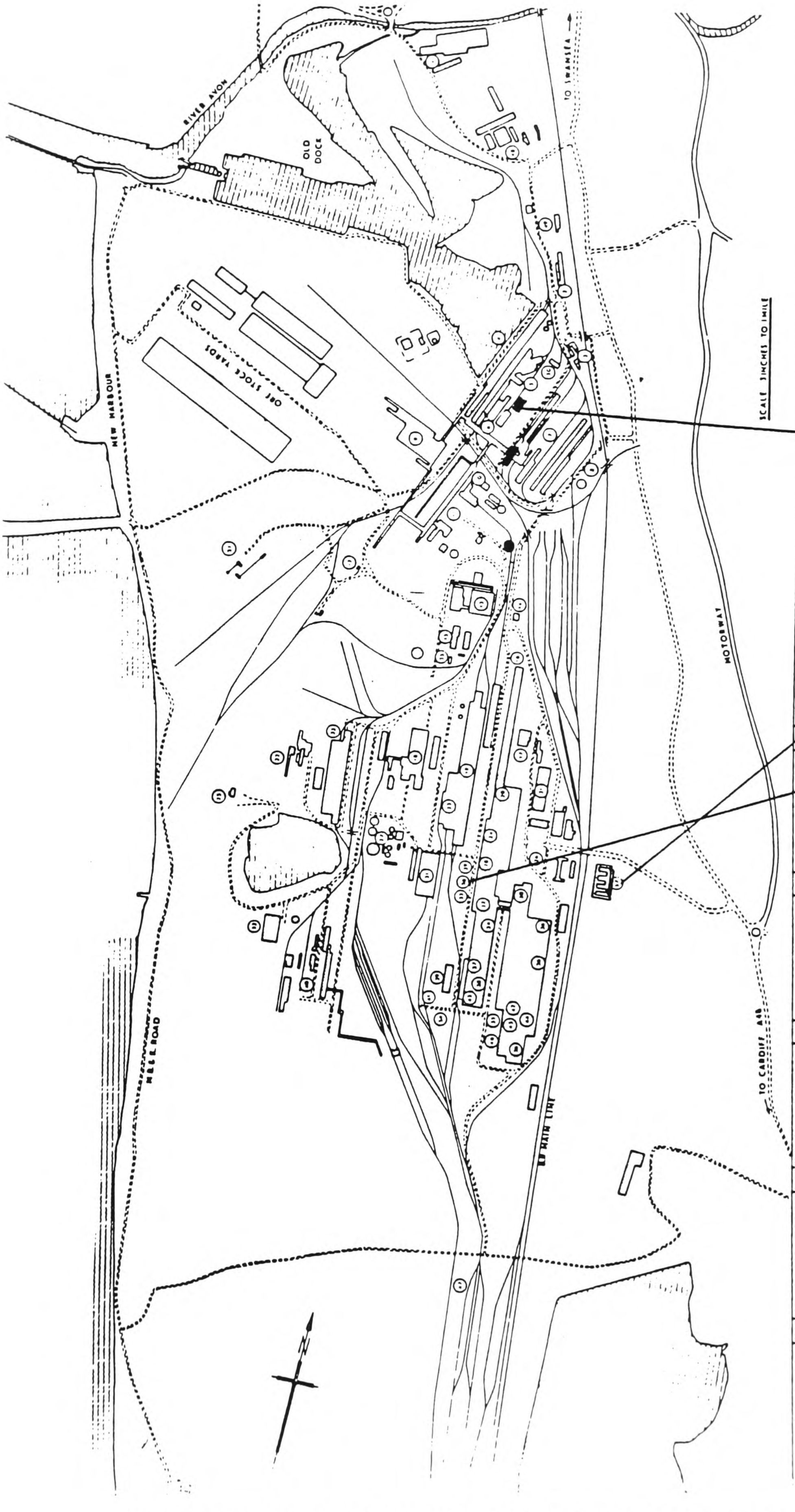


Fig. 17 General Arrangement of Level Gauges



	EXPORT TRANSIT SHED	2	FFRWDWYLLT STORES	3	GENERAL STORES MARGAM	4	MARGAM WHARF	5	Nos 1 2 & 3 BLAST FURNACES	6	A POWER PLANT	7	230 COKE OVENS	8	ROAD WEIGHBRIDGE PENRHYN	9	SINTER PLANT	10	B POWER PLANT
	Nos 4 & 5 BLAST FURNACES	12	ROAD WEIGHBRIDGE MORFA BANK	13	C E S	14	DIESEL LOCO SHED	15	CARPENTERS SHOP	16	INGOT STRIPPING	17	PLANT & VEHICLE WORKSHOPS	18	V L N	19	ABBEY MELTING SHOP	20	UNIVERSAL SLABBING MILL
	GENERAL STORES ABBEY	22	HECKETTS BASIC SLAG PLANT	23	SPLICERS SHOP	24	HOT STRIP MILL	25	HECKETTS WALES LTD	26	ROAD CONTROL POINT	27	WATER TREATMENT PLANT	28	HOT MILL ROLL SHOP	29	OIL STORES	30	HR COIL DESPATCH BAY 21
	BRICK STORES ABBEY	32	COILERS	33	SERVICES BOILER HOUSE	34	HR COIL DESPATCH BAY 6	35	HYDROCHLORIC ACID PLANT	36	COIL MILL DESPATCH BAYS 13, 15, 16, 17, 18	37	DRACONZIN DESPATCH BAY 1	38	HOT SHEET FINISHING DESPATCH BAYS 1 2 5	39	DRACONITE DESPATCH	40	CHANCE COKE OVENS BO
	SCRAP YARD	42	3 STAND COLD REDUCTION MILL	43	SECONDS SHEET STOCK BAY 1	44	COLD MILL ROLL SHOP	45	5 STAND COLD REDUCTION MILL	46	PICKLE COIL DESPATCH BAY 12	47	SOUTH SIDINGS	4	PORT TALBOT CHEMICAL CO.	49	WAGON SHOP	50	PAINT SHOP
	MARGAM SLAG COMPANY	52	NEW MECHANICAL STORES	53	BOS PLANT	54	HEAD OFFICE STRIP MILL DIV	55	HEAD OFFICE ENG SERVICES DIV	56	MEDICAL BLOCK	57	RESEARCH BLOCK		compound				

Fig. 18 Site Plan of British Steel Strip Products Group: Port Talbot Works

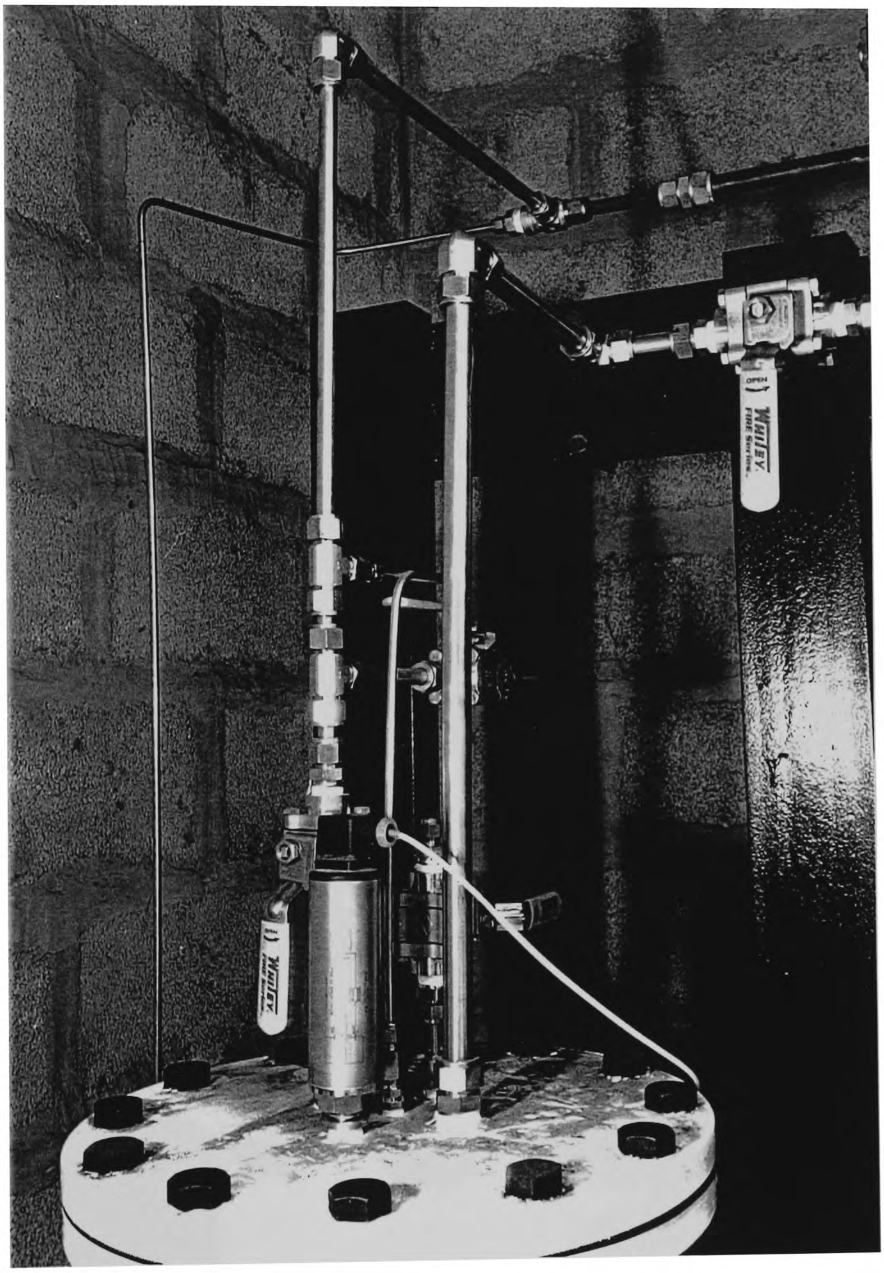


Fig. 19 Arrangement at Top of Crystalliser

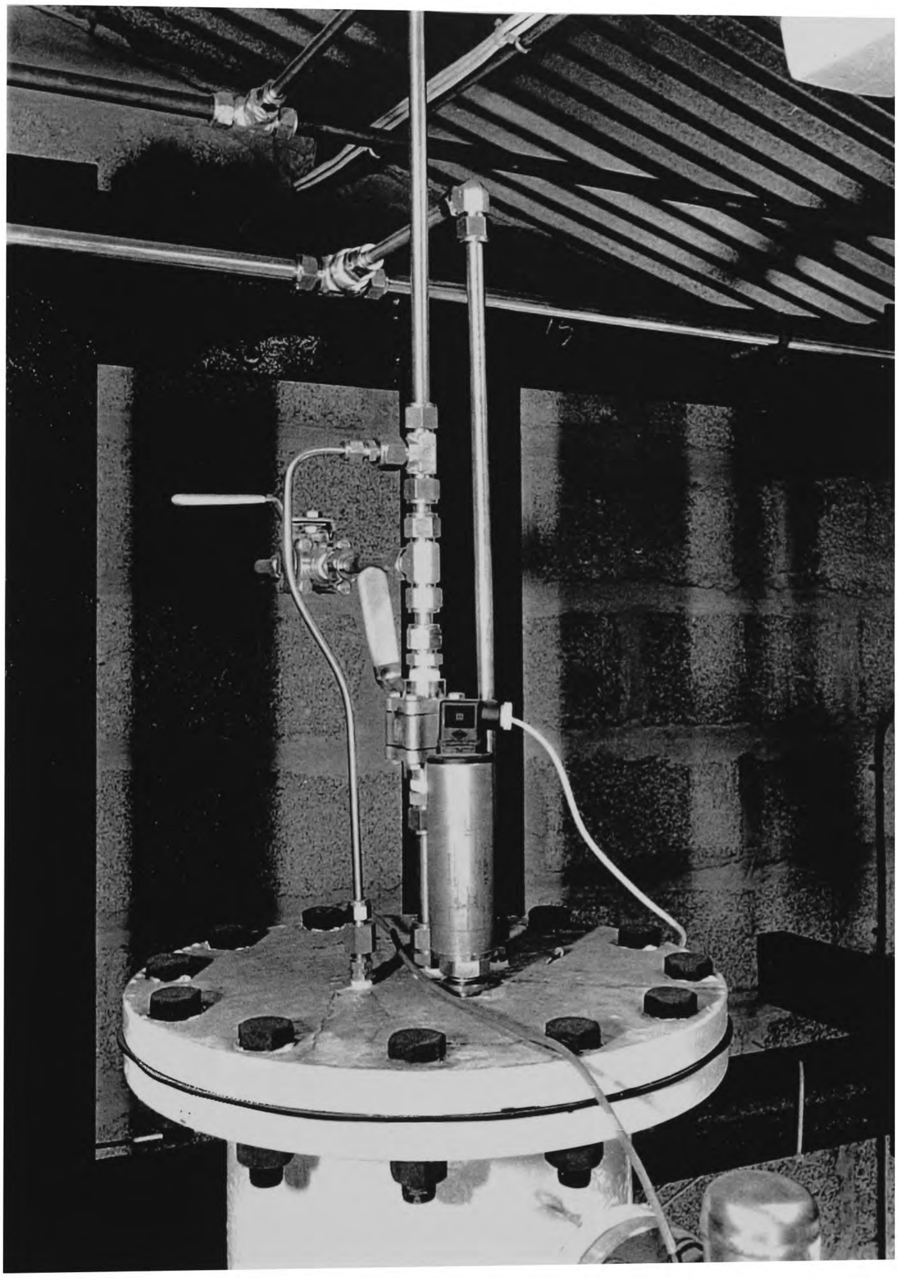


Fig. 20 Arrangement at Top of Flash Vessel

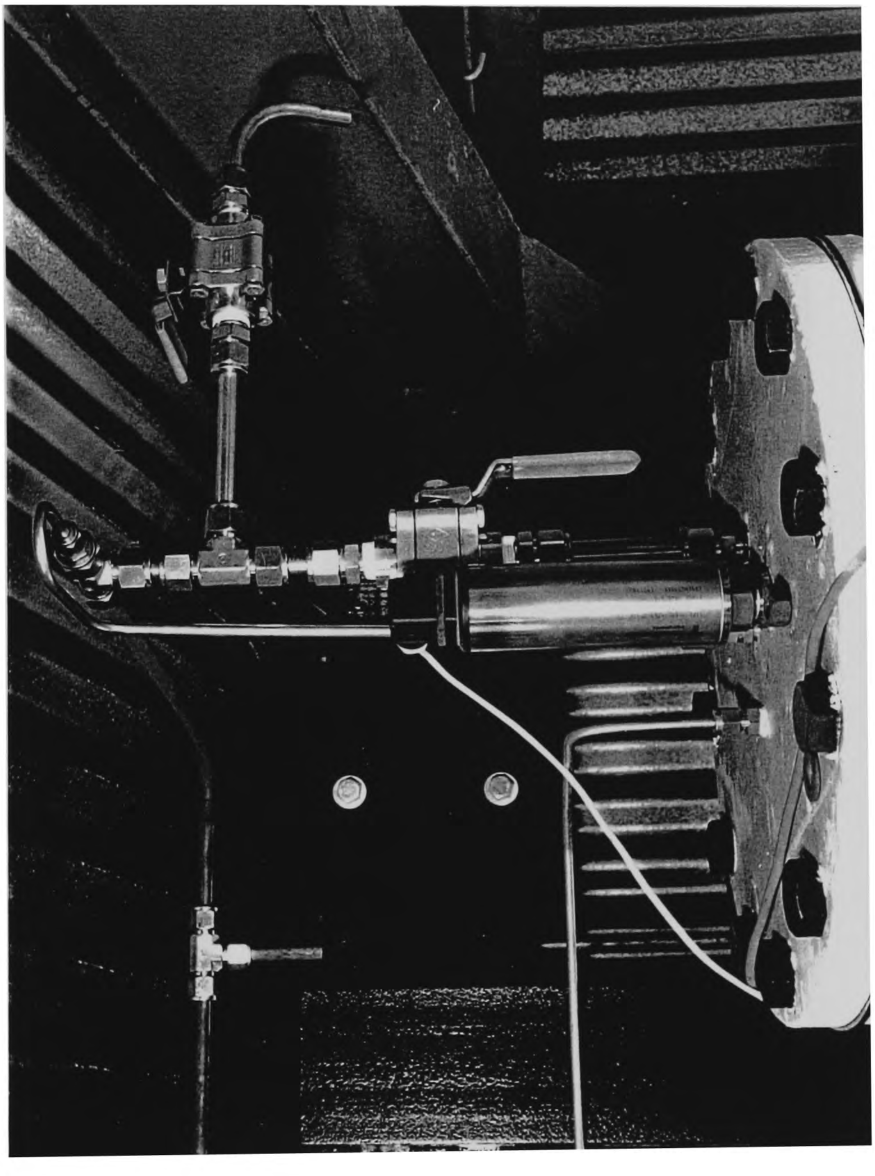


Fig. 21 Arrangement at Top of Condenser

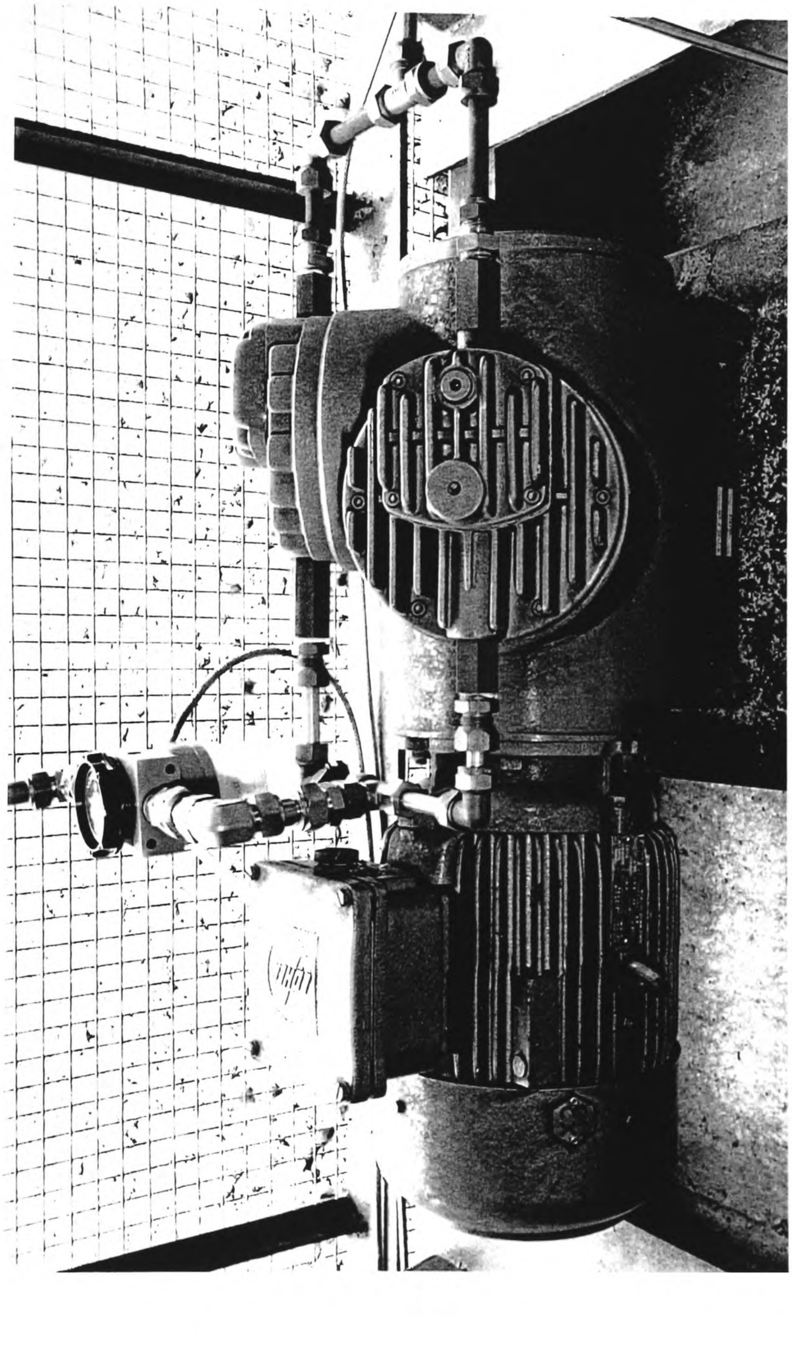


Fig. 22 Arrangement of Compressor

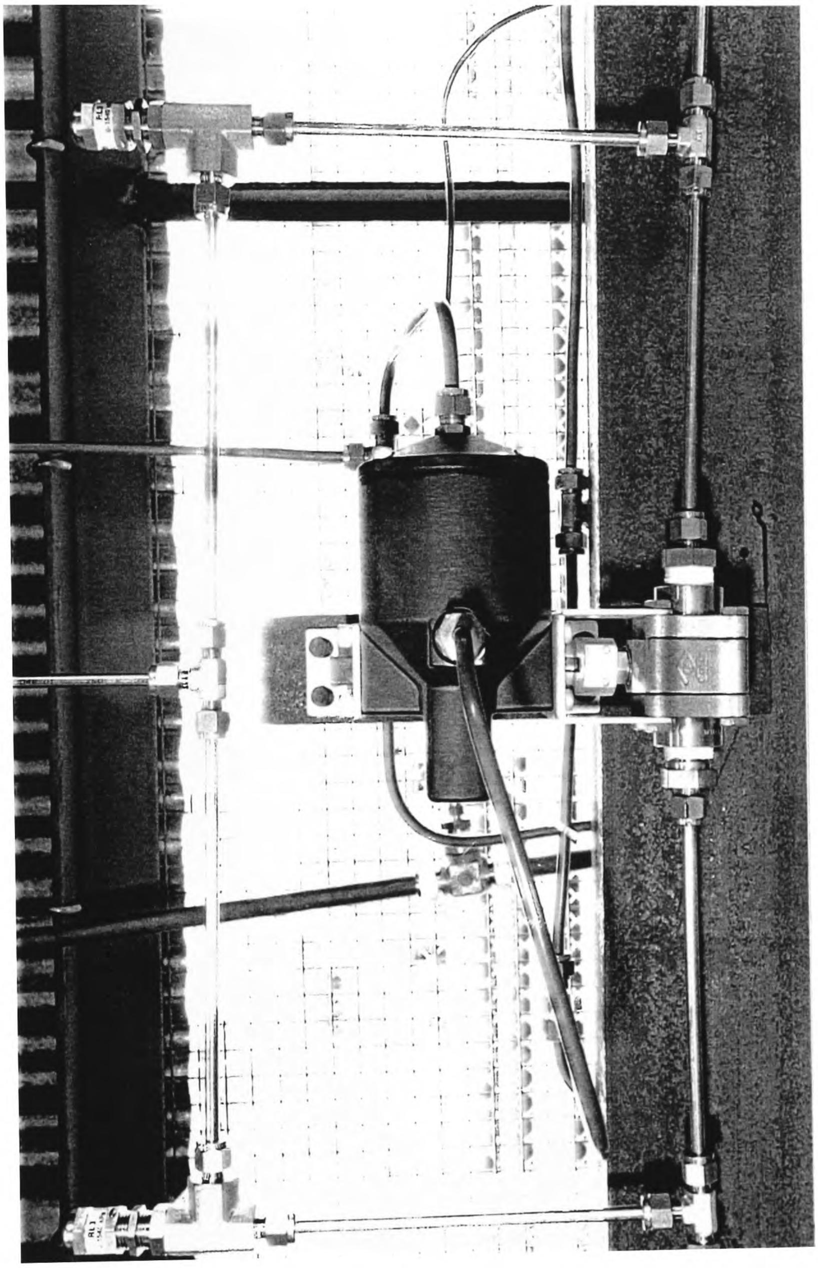


Fig. 23 Arrangement of Air-Actuated Shut-Off Valve

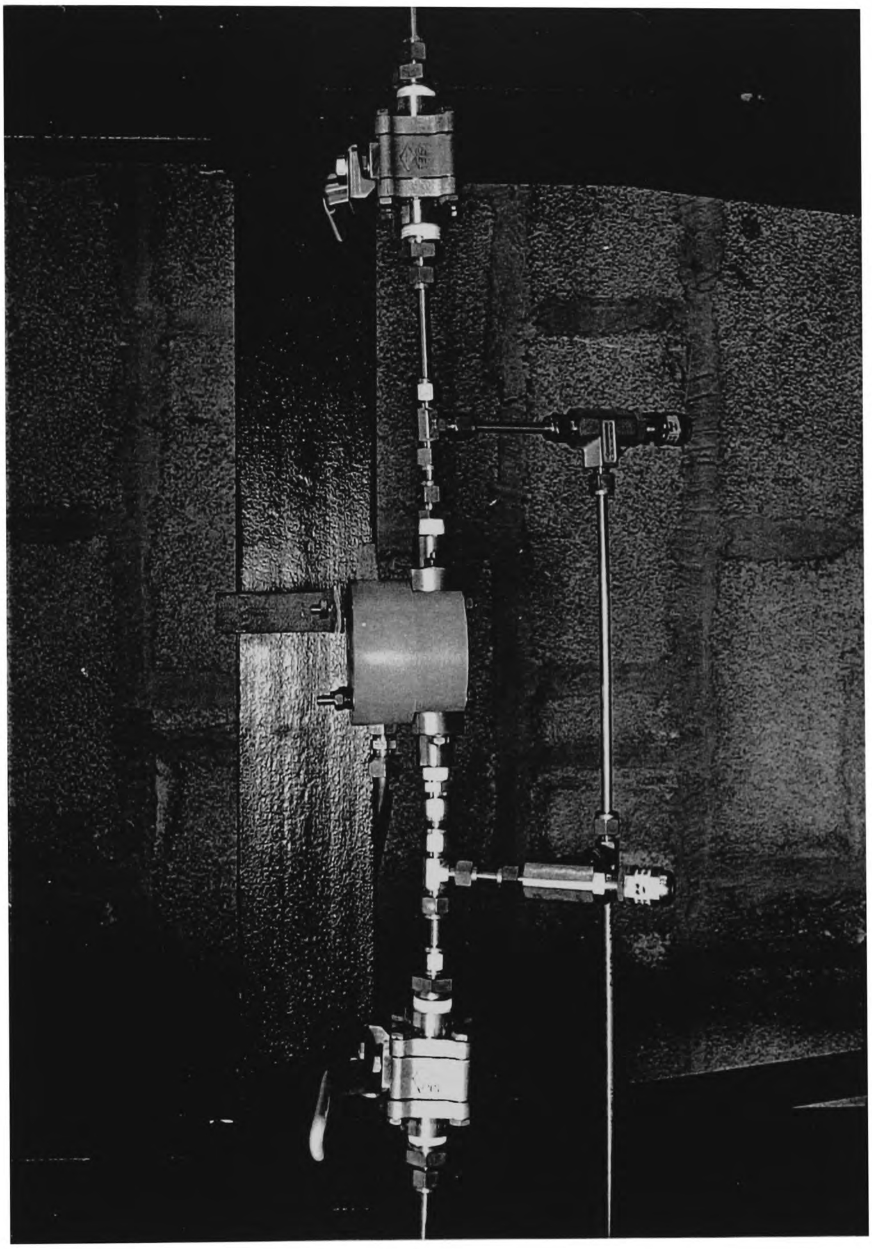


Fig. 24 Arrangement of Air Actuated Transfer Pump

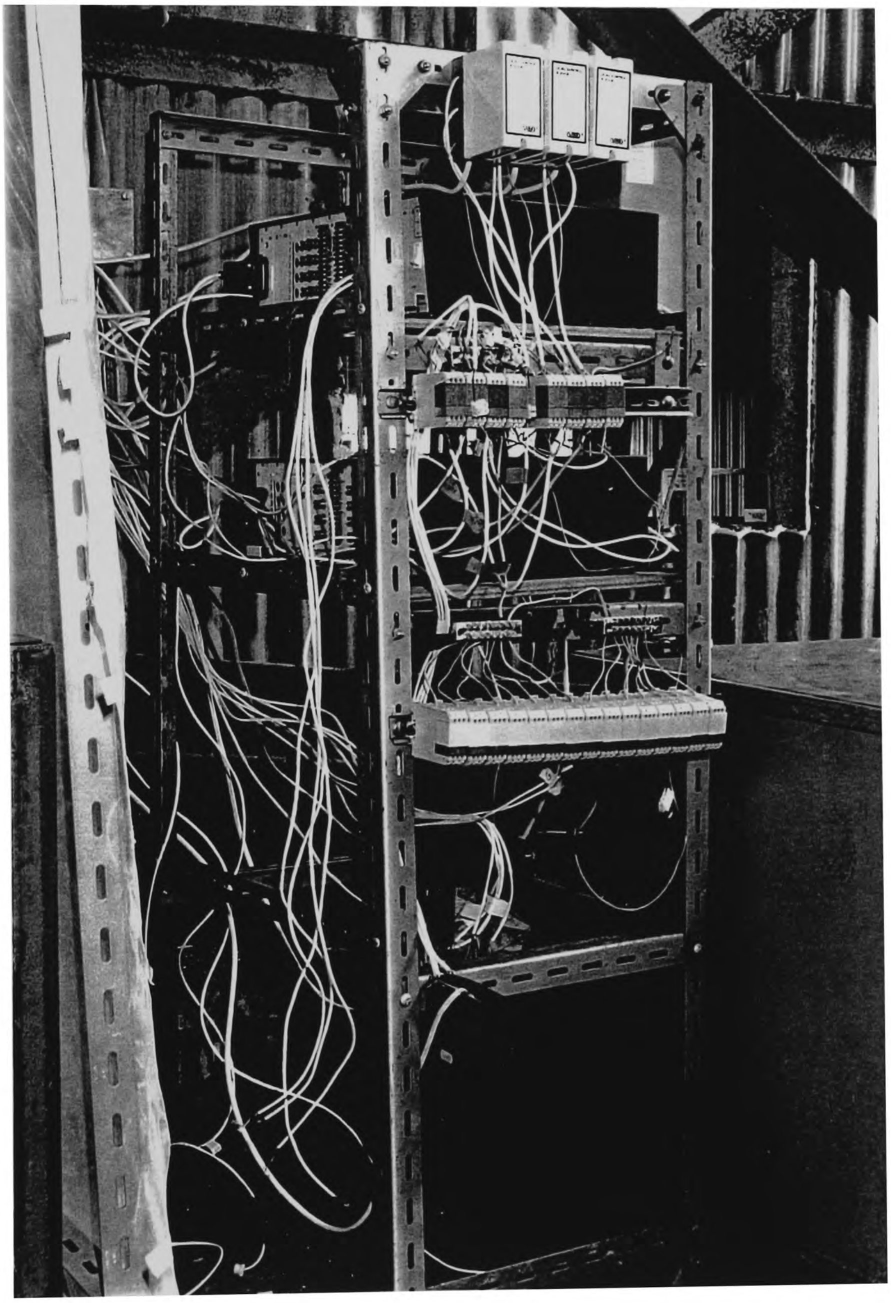


Fig. 25 Arrangement of Thinklabs and Zener Safety Barriers

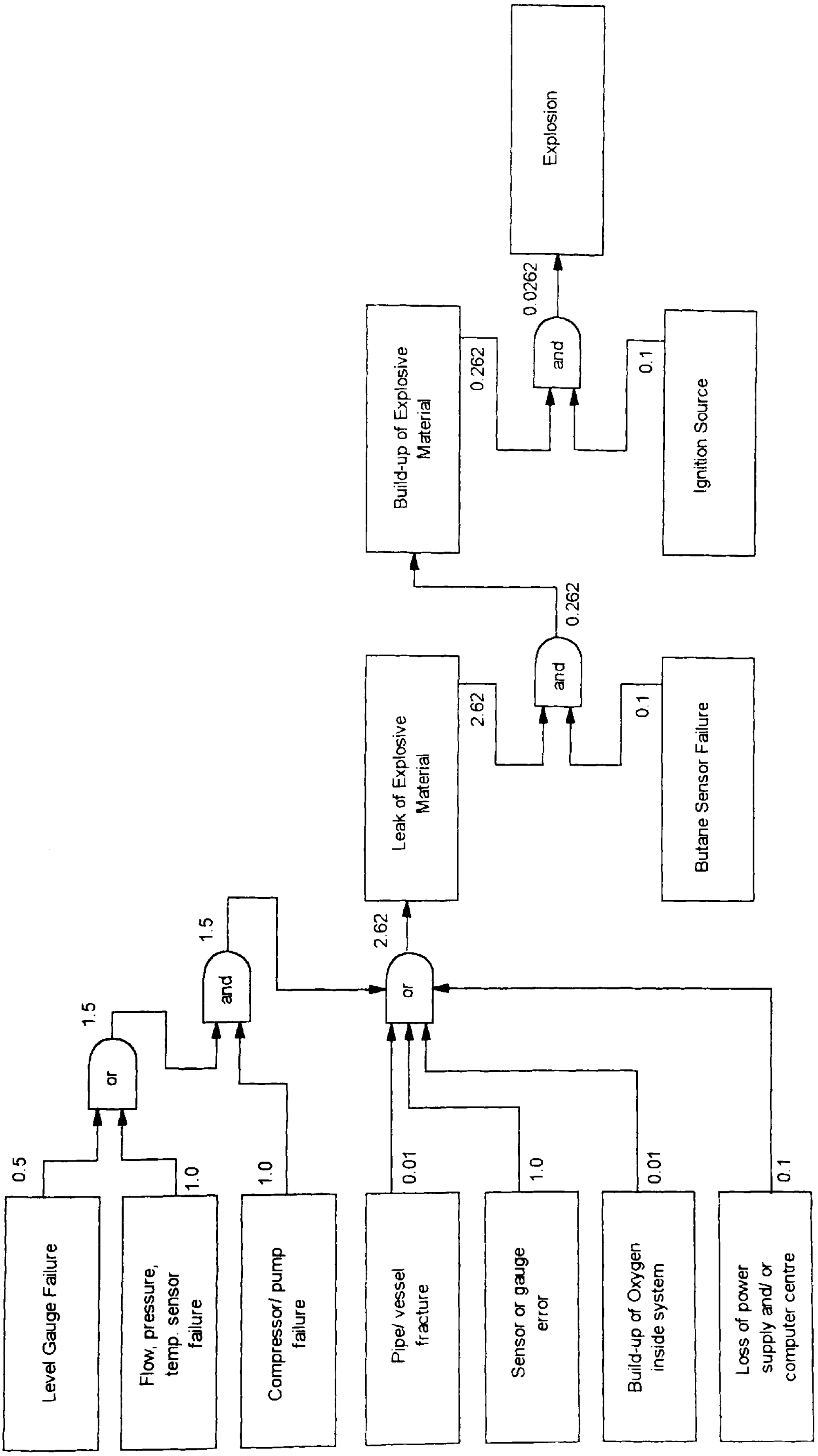


Fig. 26 Hazan Tree Analysis

Special Material, General Process and Special Process Hazards.	UNIT			
	Crystalliser	**Separator**	**Condenser**	**Flash**
Subject to detonation.	Yes	Yes	Yes	Yes
Physical changes only.	Yes	Yes	Yes	Yes
Within explosive range.	Yes	Yes	Yes	Yes
Low temperature.	Yes	Yes	Yes	Yes
Above flash point.	No	No	No	Yes
Above boiling point.	Yes	No	Yes	Yes
Greater than average explosion hazard.	Yes	Yes	Yes	Yes

Fig. 27 Special Material General Process and Special Process Hazards Associated with the Semi-Open Refrigeration Cycle

FIRE AND EXPLOSION INDEX CALCULATION SHEET	Unit :Crystalliser		
1. Material factor for : vapour / liquid Butane			19.7
2. Special Material Hazards	% factor suggested	% factor used	
a. Oxidising materials	0-20		
b. Reacts with water to produce a combustible gas	0-30		
c. Subject to spontaneous heating	30		
d. Subject to rapid spontaneous polymerisation	50-75		
e. Subject to explosive decomposition	125		
f. Subject to detonation	150	100	
g. Other	0-150		
Add percentages a-g for Special Material Hazard (SMH)	TOTAL	100	
((100 + SMH)/100 + (material factor)	= SUB TOTAL #2		39.4
3. General Process Hazards			
a Handling and physical changes only	0-50	40	
b. Continuous reactions	25-50		
c Batch reactions	25-60		
d. Multiplicity of reactions in same equipment	0-50		
Add percentages a-d for General Process Hazards (GPH)	TOTAL	40	
((100 + gph)/100)*(sub total #2)	= SUB TOTAL #3		55.2
4. Special Process Hazards			
a. Low pressure (below 1 bar)	0-100	50	
b. Operation in or near explosion range	150		
c. Low temperature 1. carbon steels (10 to -30C) 2. below -30C	15 25	5	
d. High temperature (use one only) 1. Above flash point 2. Above boiling point 3. Above auto-ignition point	10-20 25 35	25	
e. High pressure 1. 15 - 200 bar 2. Above 200 bar.	30 60		
f. Process or reactions difficult to control	50-100		
g. Dust or mist hazard	30-60		
h. Greater than average explosion hazard	60-100	30	
i. Large quantities of combustible liquids (use one only) 1. 10-25 m3 2. 25-75 m3 3. 75-200 m3 4. Above 200 m3	40-55 55-75 75-100 100+		
j. other	0-20		
add percentages a-j for Special Process Hazard (SPH)	TOTAL	110	
((100 + SPH total)/100) * sub-total #3	= FIRE AND EXPLOSION INDEX		115.9

Fig. 28 Dow Fire and Explosion Index Calculation for the Crystalliser Vessel

FIRE AND EXPLOSION INDEX CALCULATION SHEET	Unit :Condenser		
1. Material factor for : vapour / liquid Butane			19.7
2. Special Material Hazards	% factor suggested	% factor used	
a. Oxidising materials	0-20		
b. Reacts with water to produce a combustible gas	0-30		
c. Subject to spontaneous heating	30		
d. Subject to rapid spontaneous polymerisation	50-75		
e. Subject to explosive decomposition	125		
f. Subject to detonation	150	100	
g. Other	0-150		
Add percentages a-g for Special Material Hazard (SMH) TOTAL		100	
((100 + SMH)/100 + (material factor)		= SUB TOTAL #2	39.4
3. General Process Hazards			
a Handling and physical changes only	0-50	35	
b. Continuous reactions	25-50		
c Batch reactions	25-60		
d. Multiplicity of reactions in same equipment	0-50		
Add percentages a-d for General Process Hazards (GPH) TOTAL		35	
((100 + gph)/100)*(sub total #2)		= SUB TOTAL #3	53.2
4. Special Process Hazards			
a. Low pressure (below 1 bar)	0-100		
b.Operation in or near explosion range	150	30	
c. Low temperature 1. carbon steels (10 to -30°C) 2. below -30°C	15 25	5	
d. High temperature (use one only) 1. Above flash point 2. Above boiling point 3. Above auto-ignition point	10-20 25 35	0 10	
e. High pressure 1. 15 - 200 bar 2. Above 200 bar.	30 60		
f. Process or reactions difficult to control	50-100		
g. Dust or mist hazard	30-60		
h.Greater than average explosion hazard	60-100	30	
I. Large quantities of combustible liquids (use one only) 1. 10-25 m^3 2. 25-75 m^3 3. 75-200 m^3 4. Above 200 m^3	40-55 55-75 75-100 100+		
j. Other	0-20		
add percentages a-j for Special Process Hazard (SPH) TOTAL		75	
((100 + SPH total)/100) * sub-total #3		= FIRE AND EXPLOSION INDEX	93.1

Fig. 29 Dow Fire and Explosion Index Calculation for the Condenser Vessel

FIRE AND EXPLOSION INDEX CALCULATION SHEET	Unit :Separator		
1. Material factor for : vapour / liquid Butane			19.7
2. Special Material Hazards	% factor suggested	% factor used	
a. Oxidising materials	0-20		
b. Reacts with water to produce a combustible gas	0-30		
c. Subject to spontaneous heating	30		
d. Subject to rapid spontaneous polymerisation	50-75		
e. Subject to explosive decomposition	125		
f. Subject to detonation	150	50	
g. Other	0-150		
Add percentages a-g for Special Material Hazard (SMH) TOTAL		50	
((100 + SMH)/100 + (material factor)		= SUB TOTAL #2	29.6
3. General Process Hazards			
a Handling and physical changes only	0-50	5	
b. Continuous reactions	25-50		
c Batch reactions	25-60		
d. Multiplicity of reactions in same equipment	0-50		
Add percentages a-d for General Process Hazards (GPH) TOTAL		5	
((100 + gph)/100)*(sub total #2)		= SUB TOTAL #3	31.1
4. Special Process Hazards			
a. Low pressure (below 1 bar)	0-100		
b. Operation in or near explosion range	150	10	
c. Low temperature 1. carbon steels (10 to -30°C) 2. below -30°C	 15 25		
d. High temperature (use one only) 1. Above flash point 2. Above boiling point 3. Above auto-ignition point	 10-20 25 35		
e. High pressure 1. 15 - 200 bar 2. Above 200 bar.	 30 60		
f. Process or reactions difficult to control	50-100		
g. Dust or mist hazard	30-60		
h. Greater than average explosion hazard	60-100	10	
i. Large quantities of combustible liquids (use one only) 1. 10-25 m^3 2. 25-75 m^3 3. 75-200 m^3 4. Above 200 m^3	 40-55 55-75 75-100 100+		
j. Other	0-20		
add percentages a-j for Special Process Hazard (SPH) TOTAL		20	
((100 + SPH total)/100) * sub-total #3	= FIRE AND EXPLOSION INDEX		37.3

Fig. 30 Dow Fire and Explosion Index Calculation for the Separator Vessel

FIRE AND EXPLOSION INDEX CALCULATION SHEET	**Unit : Flash Vaporisation**		
1. Material factor for : vapour / liquid Butane			19.7
2. Special Material Hazards	% factor suggested	% factor used	
a. Oxidising materials	0-20		
b. Reacts with water to produce a combustible gas	0-30		
c. Subject to spontaneous heating	30		
d. Subject to rapid spontaneous polymerisation	50-75		
e. Subject to explosive decomposition	125		
f. Subject to detonation	150	100	
g. Other	0-150		
Add percentages a-g for Special Material Hazard (SMH)	TOTAL	100	
((100 + SMH)/100 + (material factor)	= SUB TOTAL #2		39.4
3. General Process Hazards			
a. Handling and physical changes only	0-50	50	
b. Continuous reactions	25-50		
c Batch reactions	25-60		
d. Multiplicity of reactions in same equipment	0-50		
Add percentages a-d for General Process Hazards (GPH)	TOTAL	50	
((100 + gph)/100)*(sub total #2)	= SUB TOTAL #3		59.1
4. Special Process Hazards			
a. Low pressure (below 1 bar)	0-100	50	
b. Operation in or near explosion range	150		
c. Low temperature 1. carbon steels (10 to -30C) 2. below -30C	15 25	5	
d. High temperature (use one only) 1. Above flash point 2. Above boiling point 3. Above auto-ignition point	10-20 25 35	20	
e. High pressure 1. 15 - 200 bar 2. Above 200 bar.	30 60		
f. Process or reactions difficult to control	50-100		
g. Dust or mist hazard	30-60		
h. Greater than average explosion hazard	60-100	30	
I. Large quantities of combustible liquids (use one only) 1. 10-25 m3 2. 25-75 m3 3. 75-200 m3 4. Above 200 m3	40-55 55-75 75-100 100+		
j. other	0-20		
add percentages a-j for Special Process Hazard (SPH)	TOTAL	105	
((100 + SPH total)/100) * sub-total #3	= FIRE AND EXPLOSION INDEX		121.2

Fig. 31 Dow Fire and Explosion Index Calculation for the Flash Vaporisation Vessel

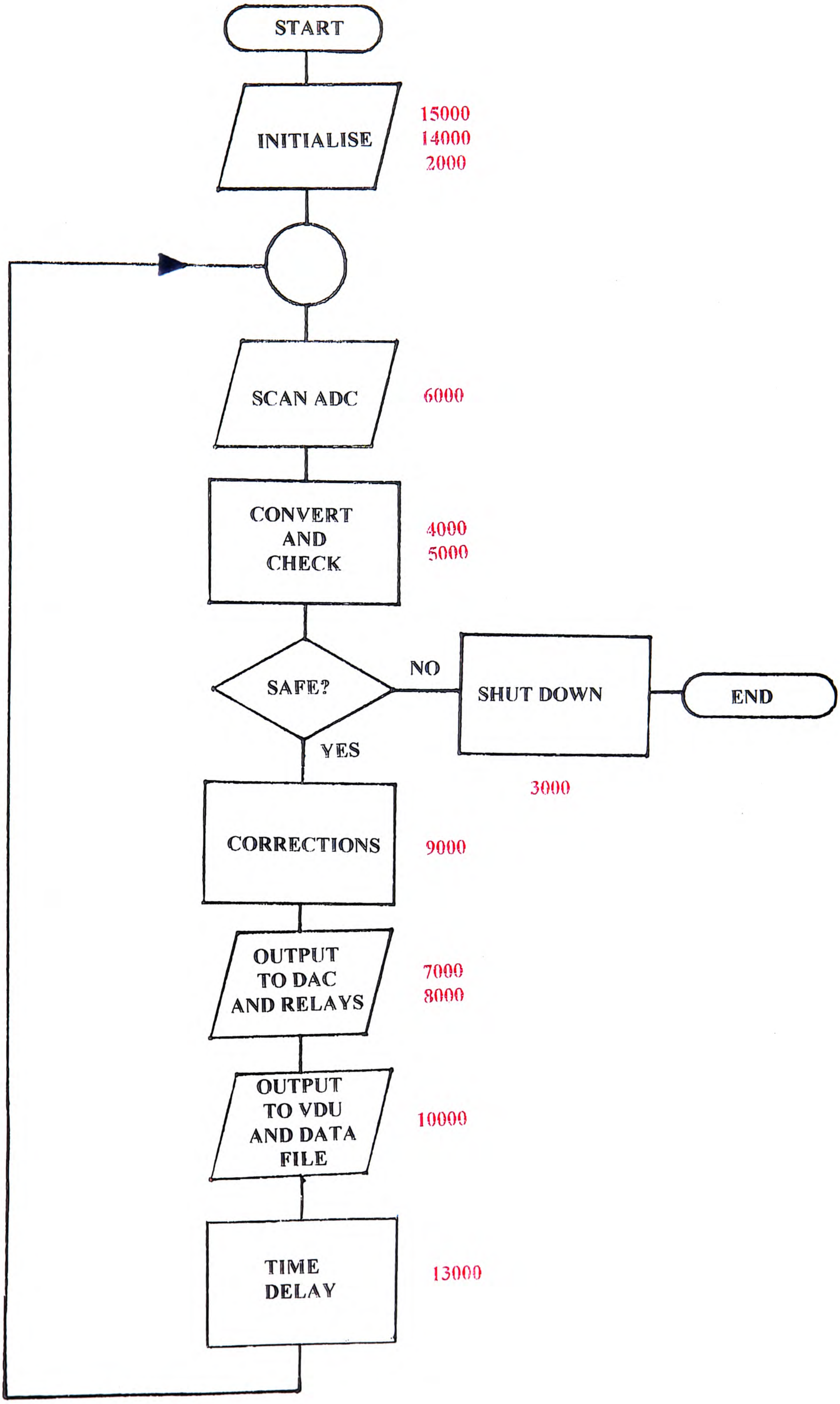


Fig. 32 Flowchart of the SORC Control Program and Major Sub-Routines

```
SORC            01-14-1990          11:16:27             40587         191
PMS, TAM, THW        7.771          11.4          45.3          45.3
flow     1,2    1.149         1.150
Ppump  1,2,3    6.722         5.826         7.293
VOLTS           1,2,3    9             8             10
0               0             1             0             2

                Crystalliser  Flash         Separator**** Condenser
Level            36.1         78.7          59.4          76.3
Press            0.483        1.226         2.523         3.022
Top-temp                                    25.1          26.0
                                                          27.0
                                                          31.6
                                                          32.2
                                                          32.0
                                                          32.0
                                                          32.1
                                                          32.9
                                                          32.1
                                                          32.5
Bottom-temp     4.9                         27.1          39.1
```

Data File:

```
56635
7.771           11.4          45.3
1.149           0             1.15          0
6.772           4.826         7.293
9               8             10
36.1            78.7          59.4          76.3
0.483           1.226         2.523         3.022
4.9             25.1          27.1          39.1
26.0            27.0          31.6          32.2          32.0
32.0            32.1          32.9          32.1          32.5
```

Key :

SORC date time seconds count scan no.
Pressure Mains Supply, Temperature AMbient, Temperature Hot Water.
Flowmeter 1,2.
Pressure to Pumps 1,2,3.
Relay actuation
Level in Units
Pressure in Units
Top Temperature
Bottom Temperature

All pressures are in bar gauge.
All temperatures are in °C.
Levels are expressed as centimetres above the base of the vessel.
Voltages are in volts.
Flowrates are in litres per minute.
**** indicates that the level switch in the separator is actuated, opening the solenoid valves to the Flash vessel.

Fig. 33 Typical Vdu Display and Data File

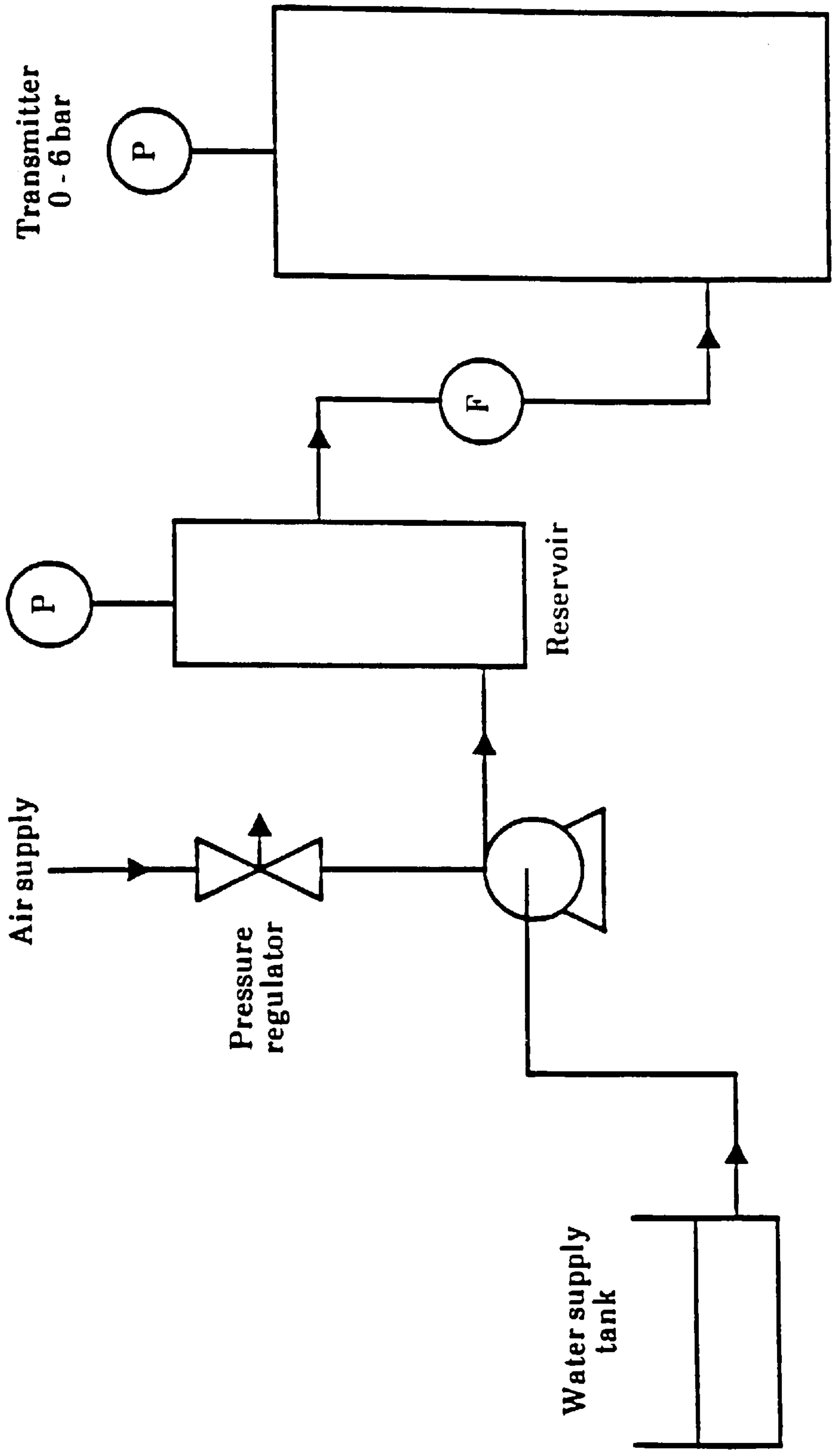


Fig. 34 Pump Calibration Arrangement

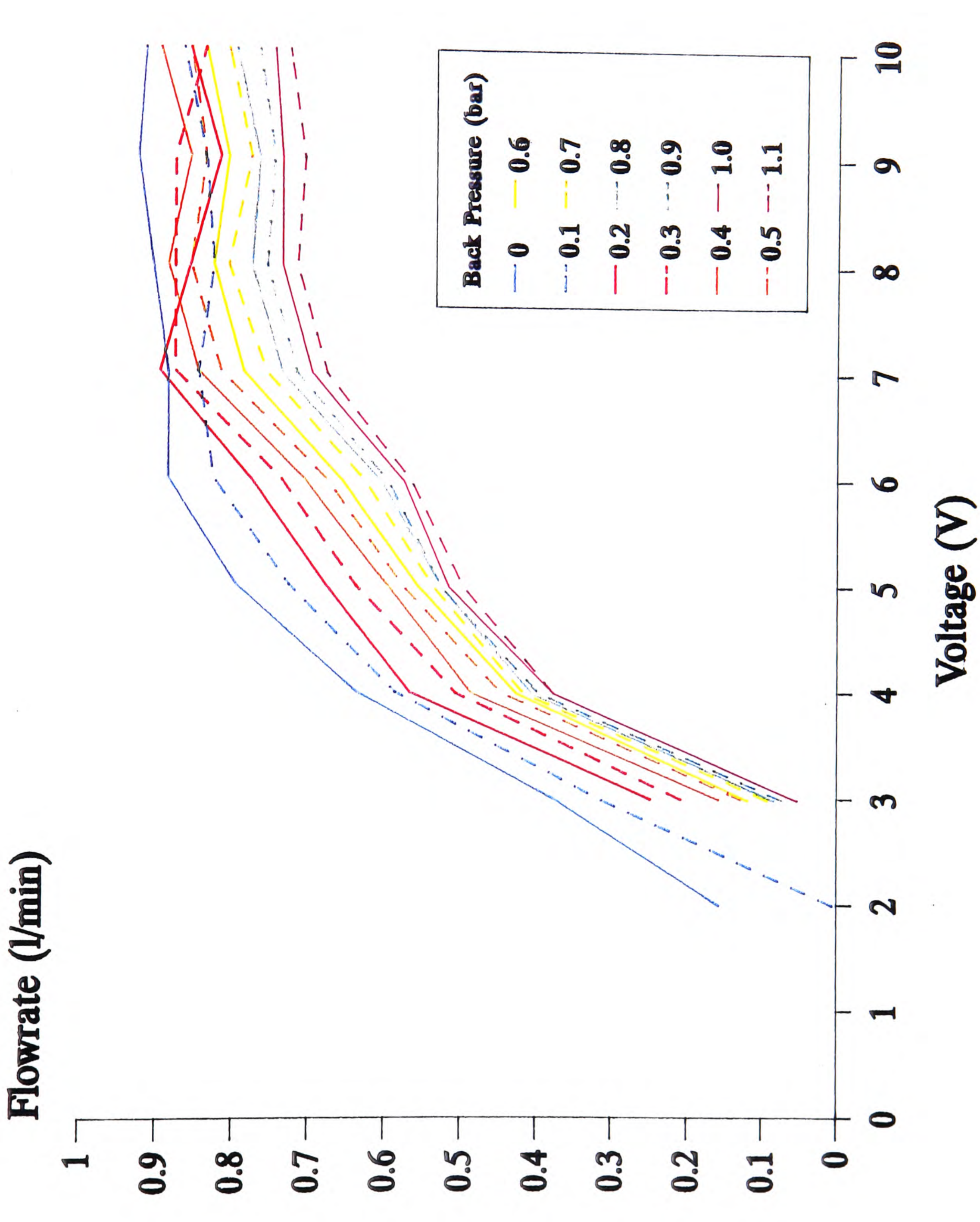


Fig. 35 Typical Pump Calibration Curves

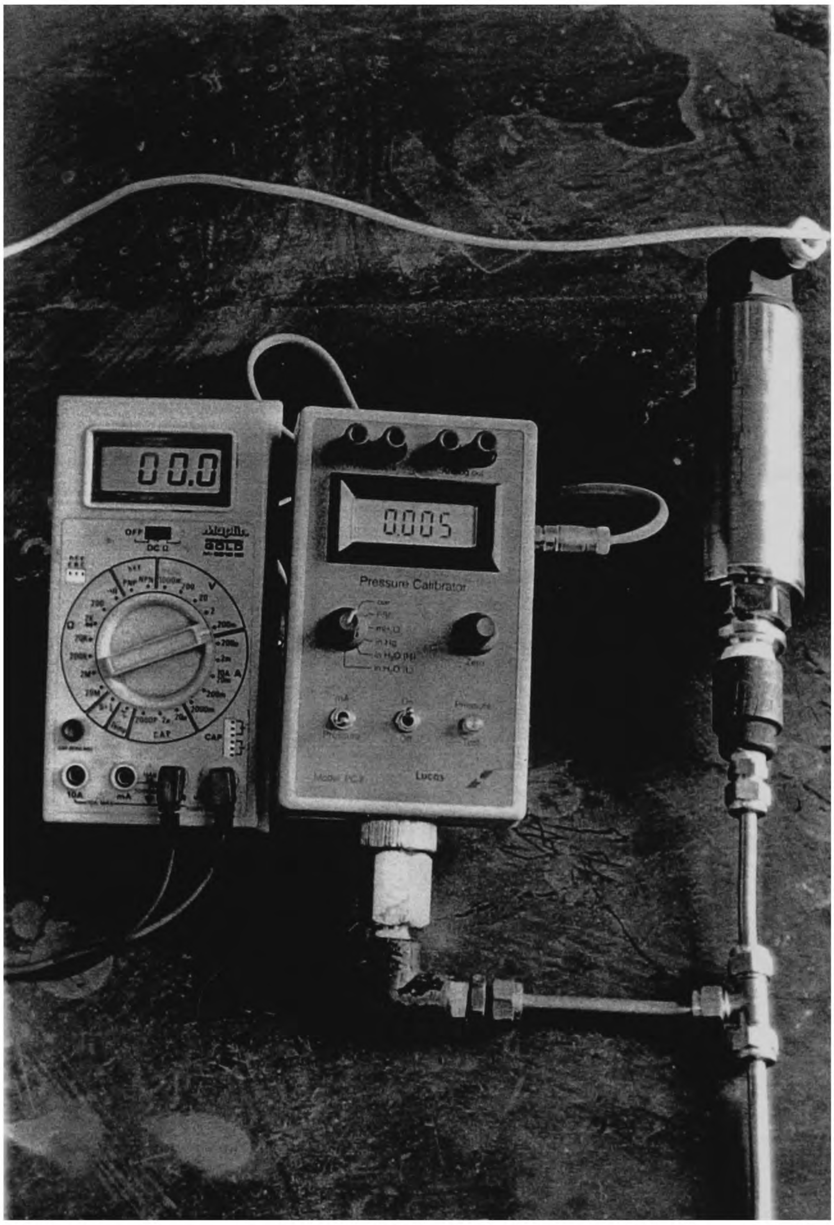


Fig. 36 Pressure Transmitter Calibration Arrangement

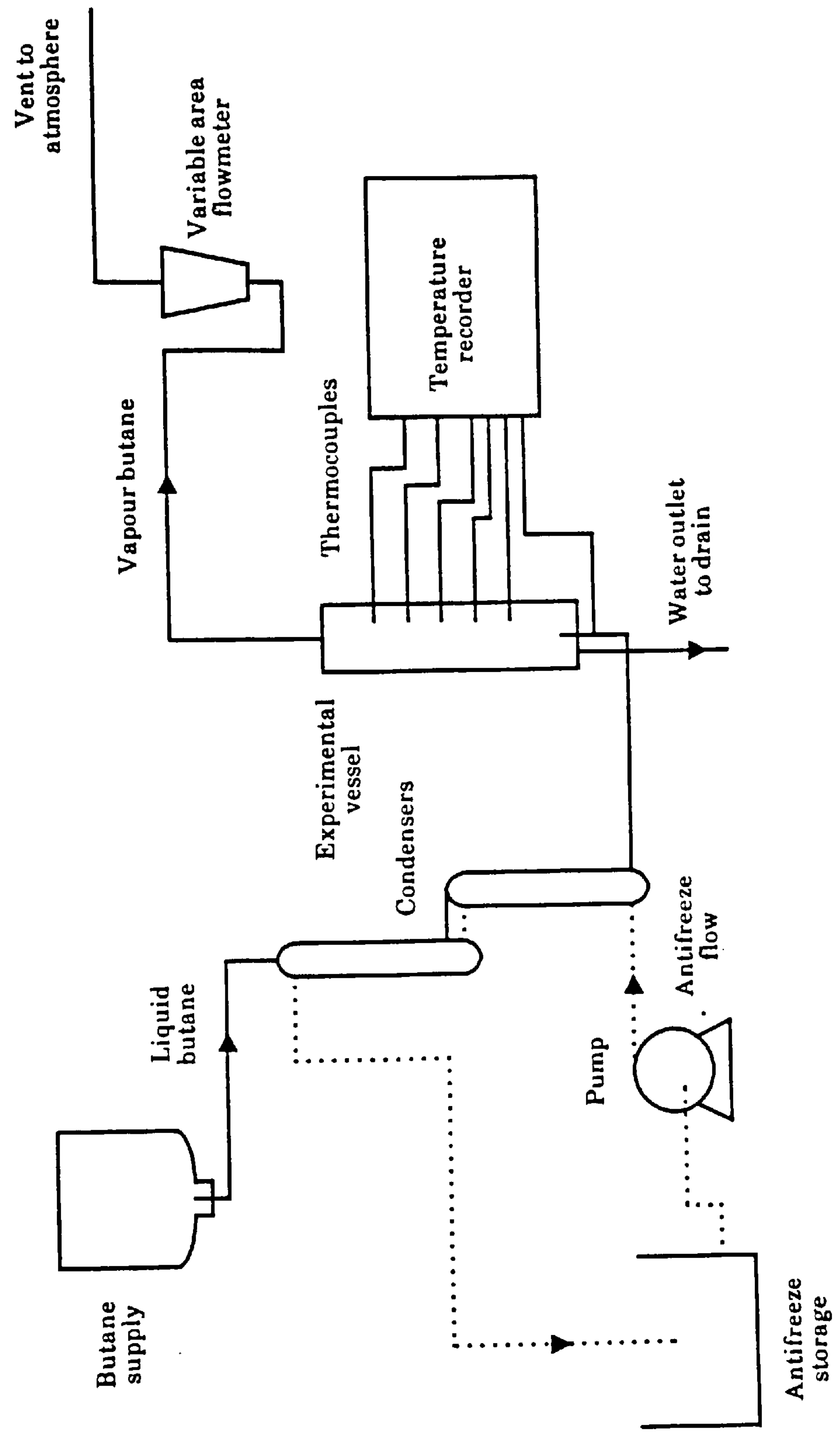


Fig. 37 Experimental Apparatus for the Evaporation of Butane

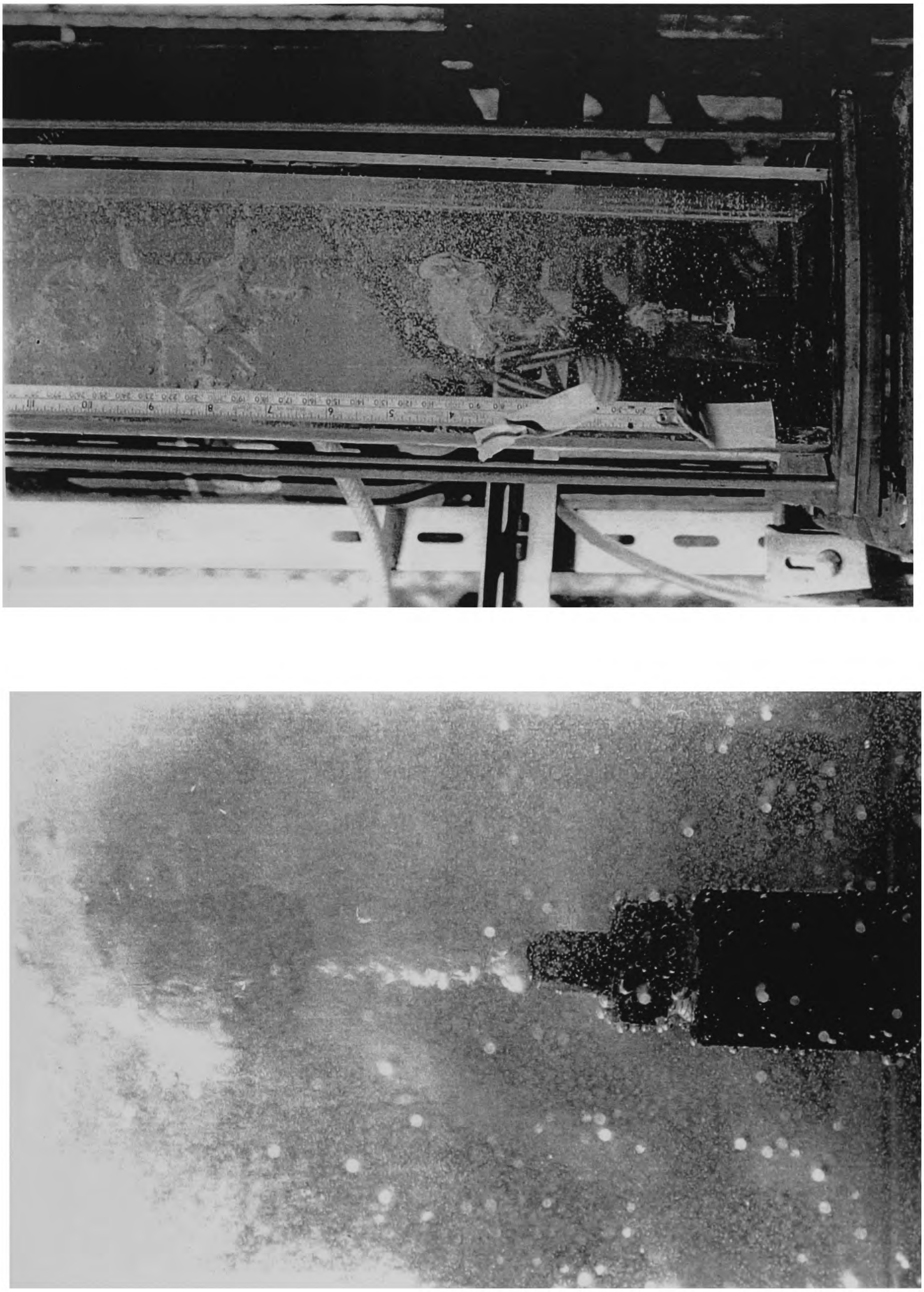


Fig. 38 Evaporation of Butane Using a Single 1mm Diameter Nozzle

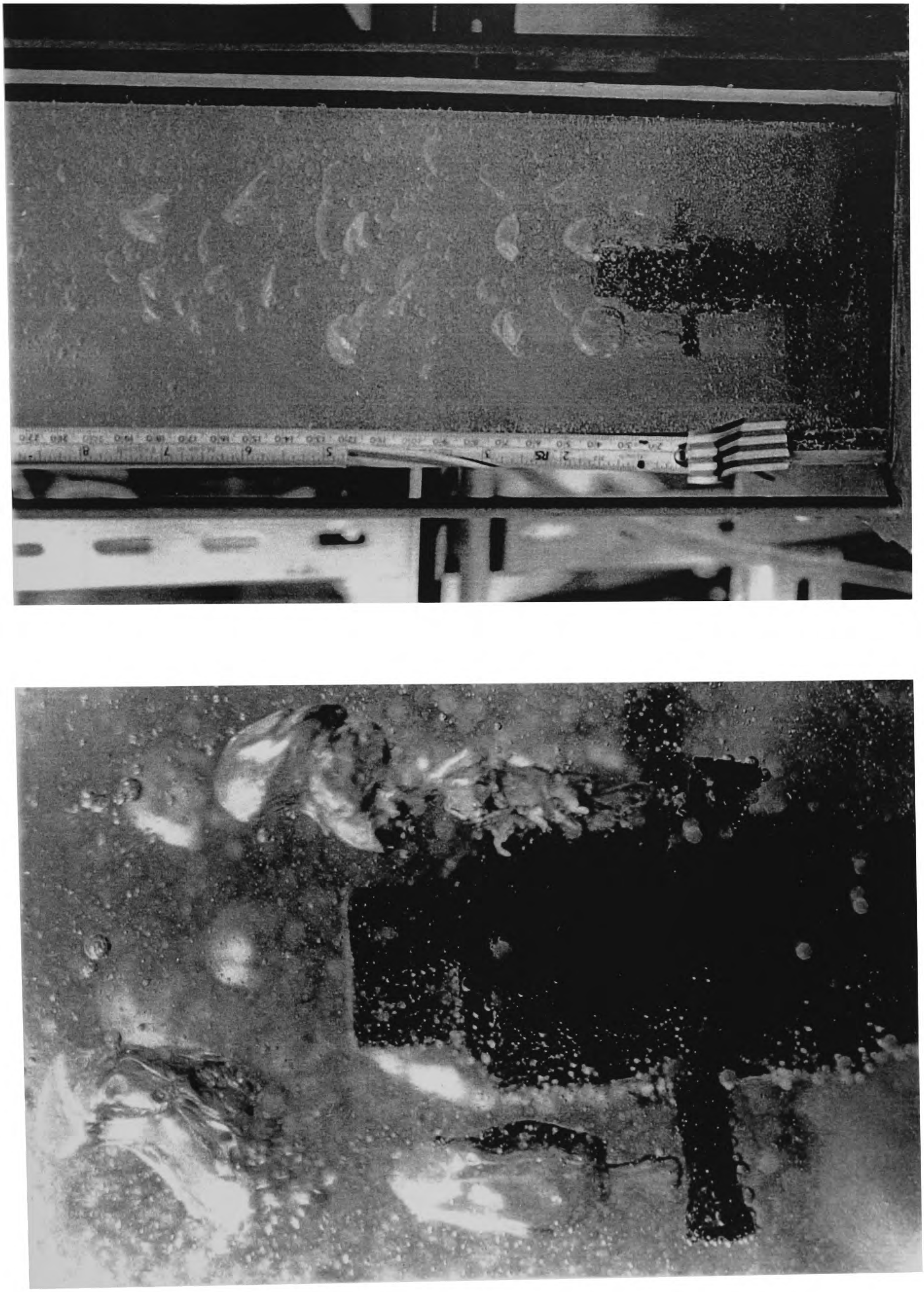


Fig. 39 Evaporation of Butane Using a Nozzle Consisting

4 Holes 0.5 mm. Diameter.

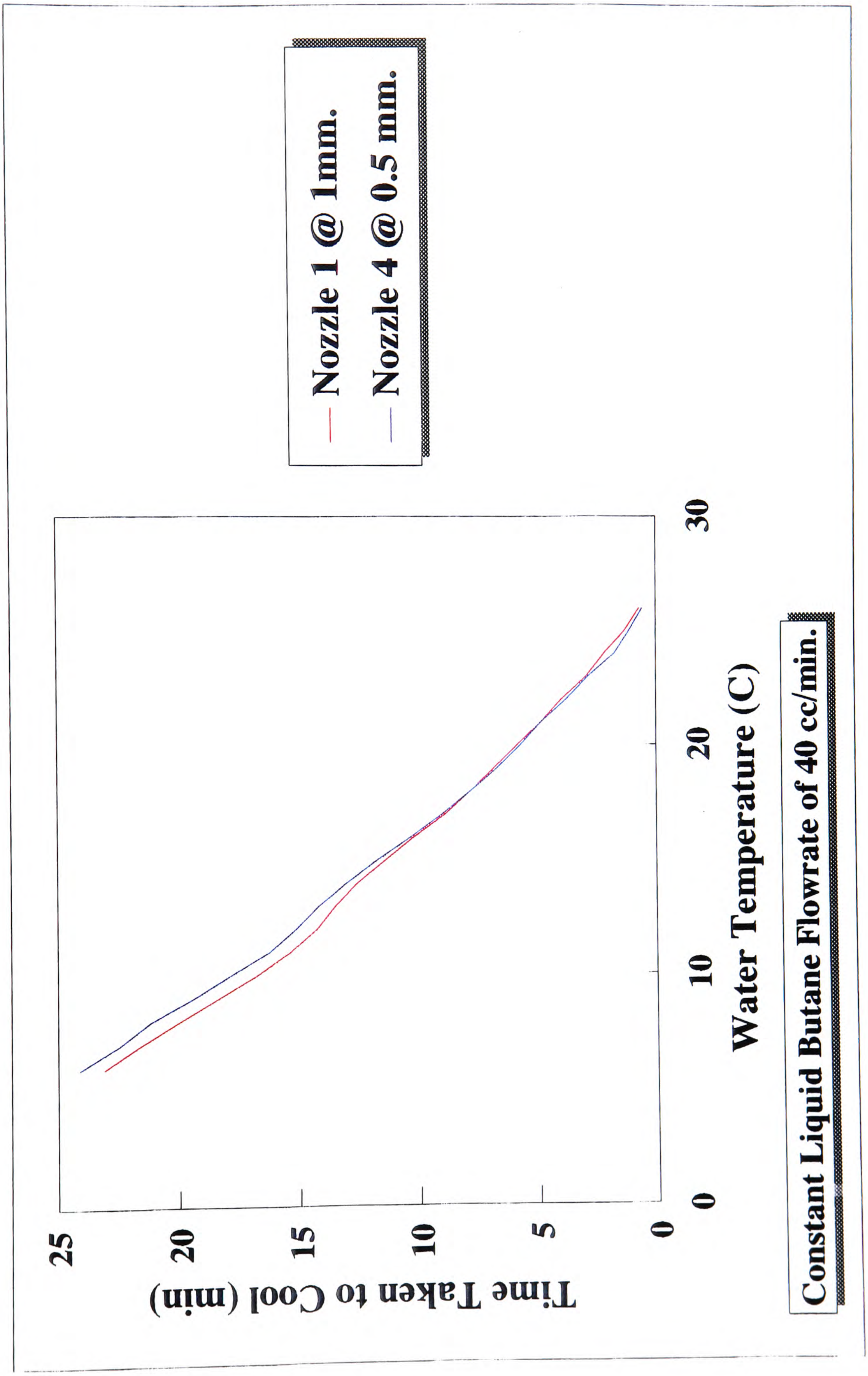
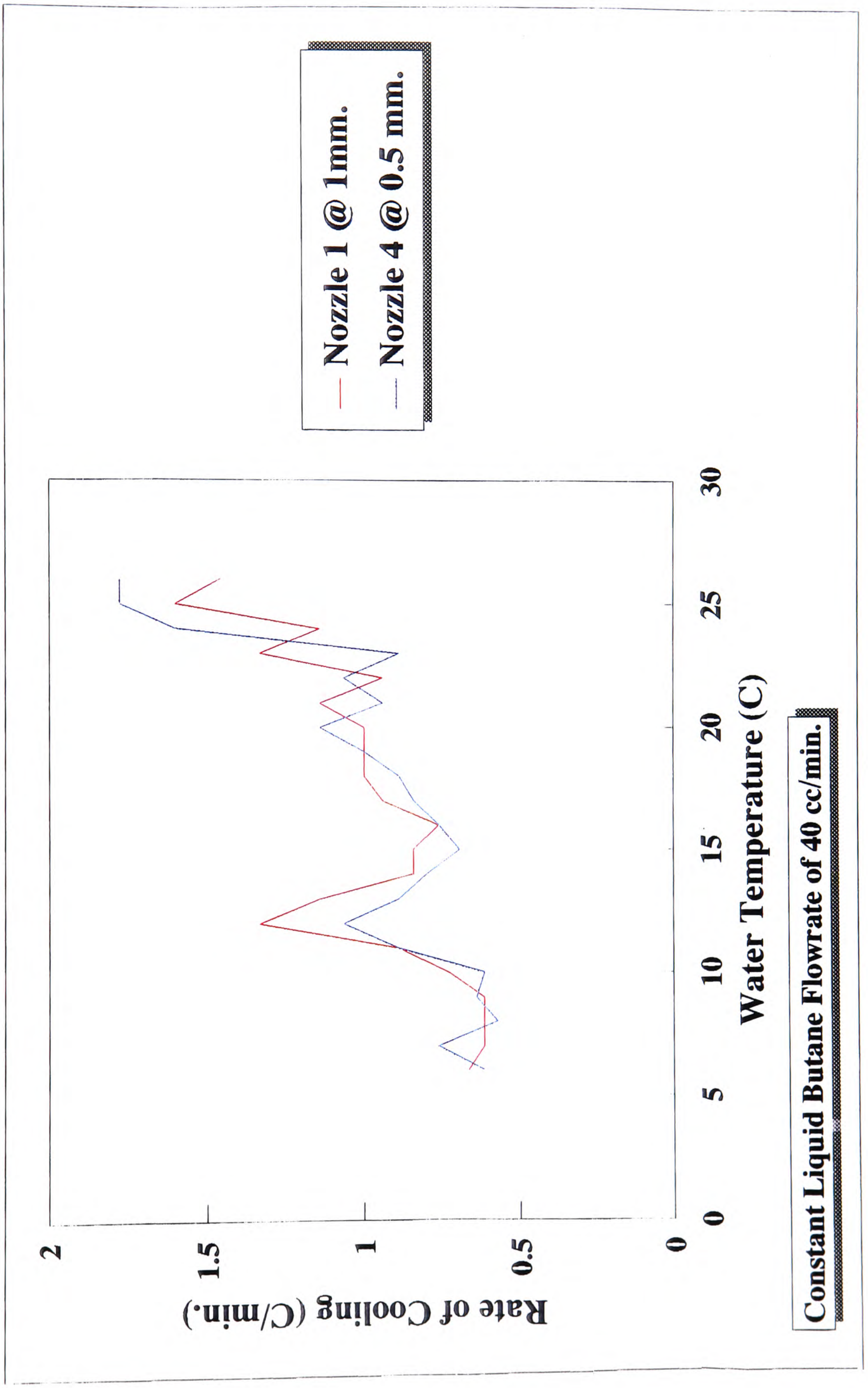


Fig. 40 Effect of Nozzle Design on Cooling Time



Constant Liquid Butane Flowrate of 40 cc/min.

Fig. 41 Effect of Nozzle Design on Rate of Cooling

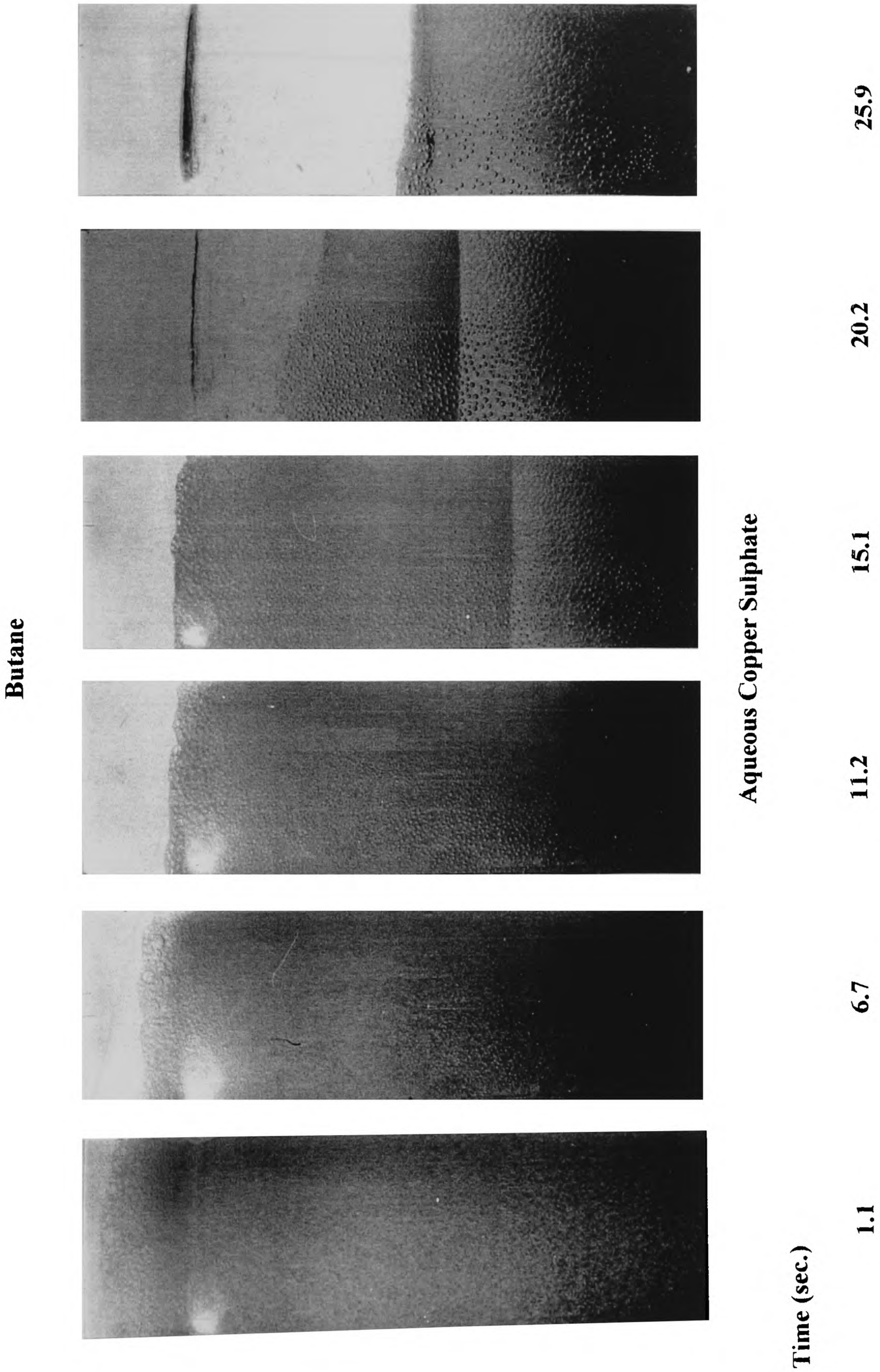


Fig. 42 Separation Test

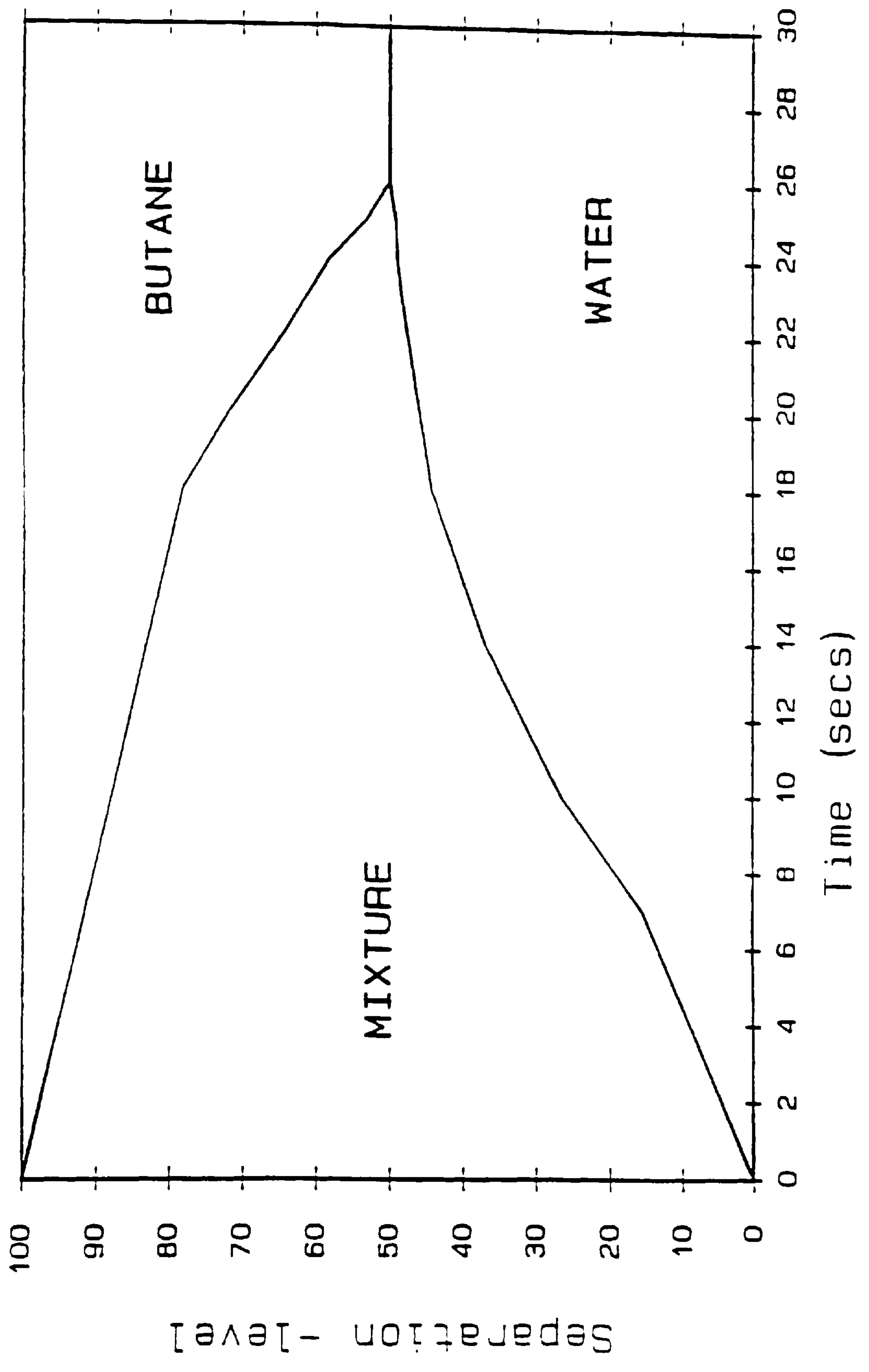


Fig. 43 Separation Rate : Water / Butane System

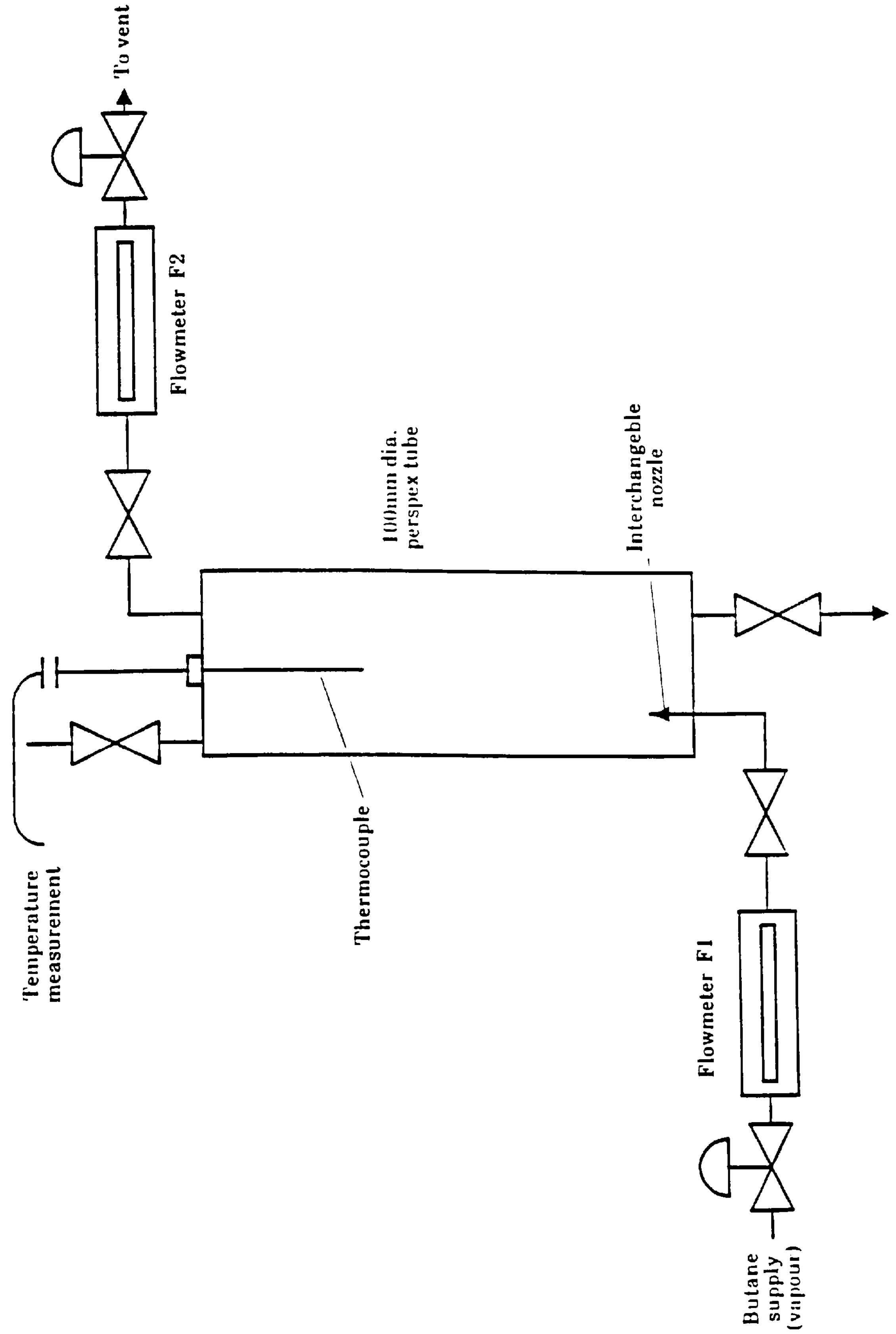


Fig. 44 Experimental Apparatus for the Condensation of Butane into Chilled Aqueous Solutions

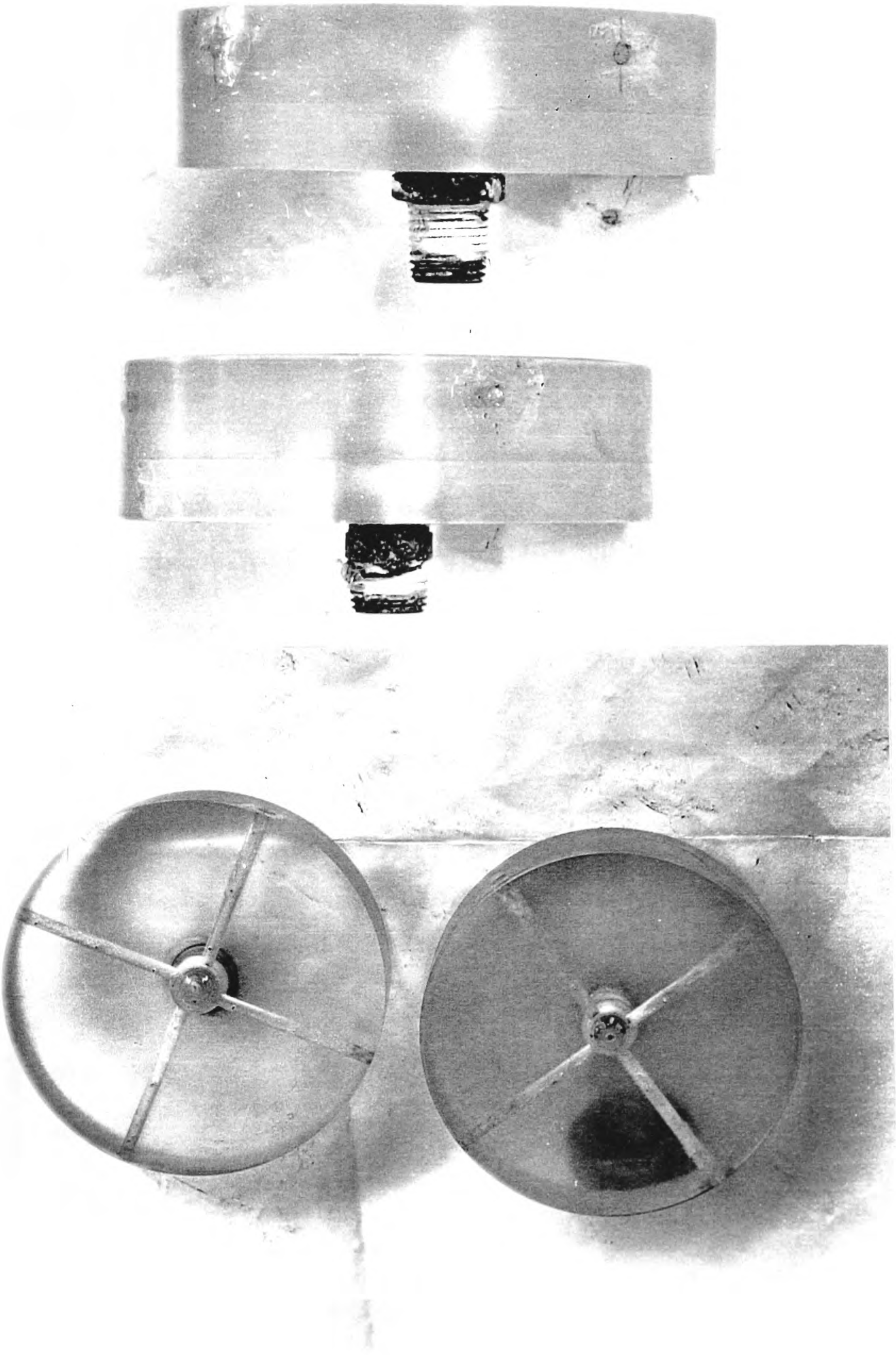


Fig. 45 Arrangement of Experimental Nozzles

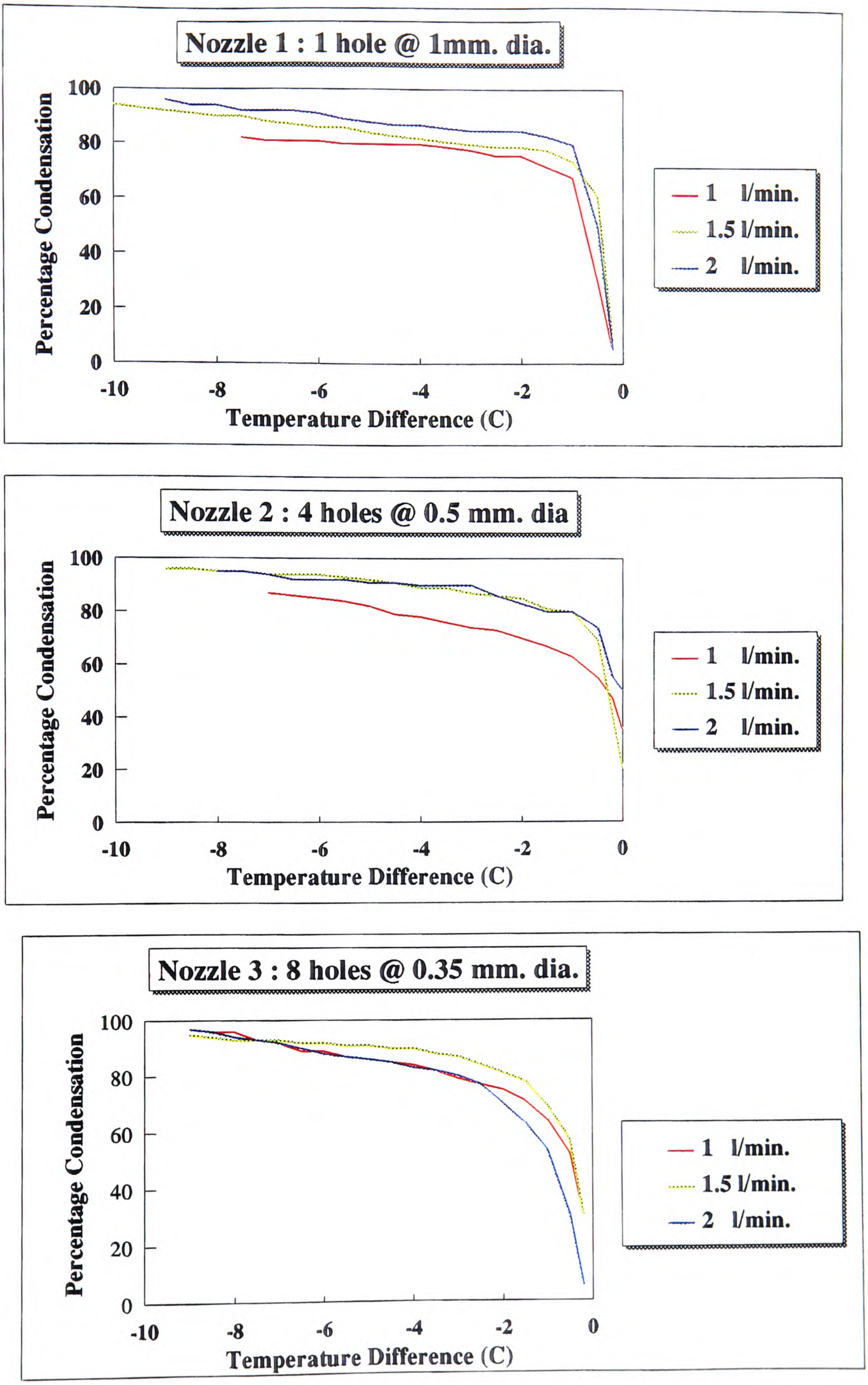
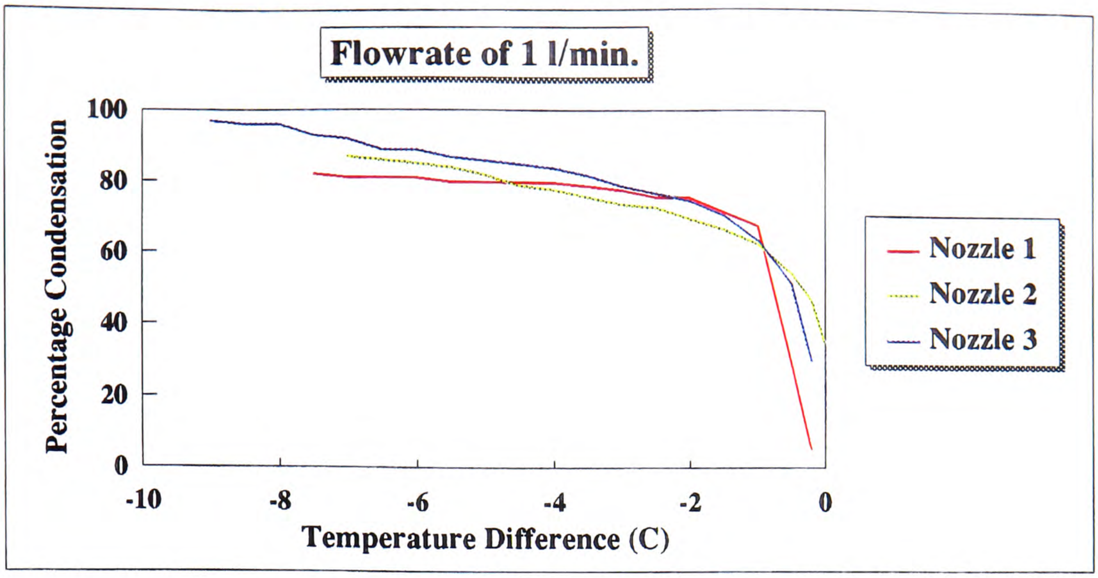
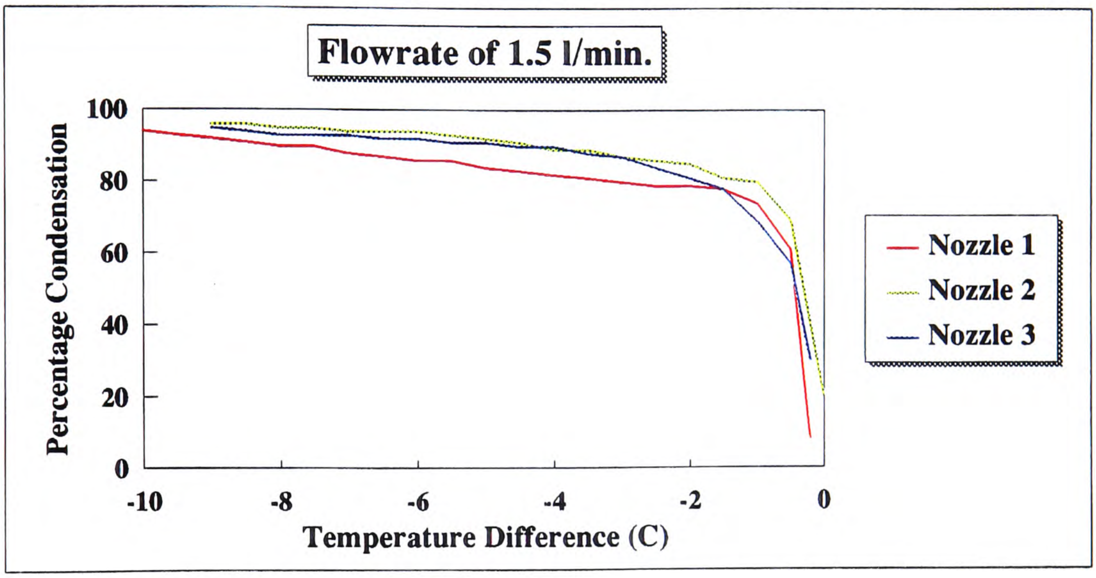


Fig. 46 Effect of Flowrate on Nozzle Performance





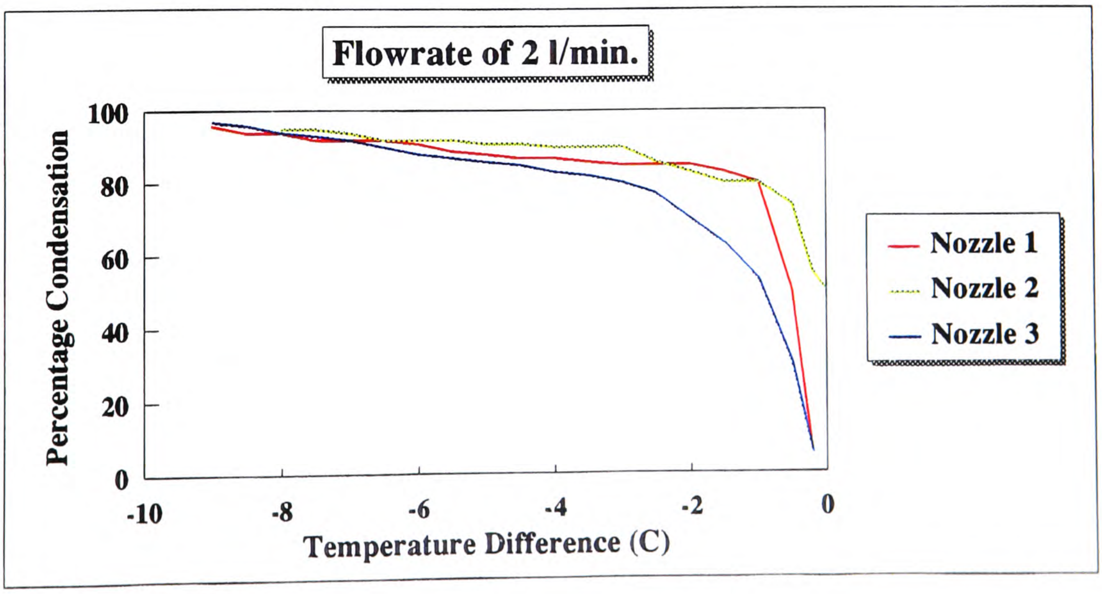


Fig. 47 Effect of Nozzle Design on Nozzle Performance

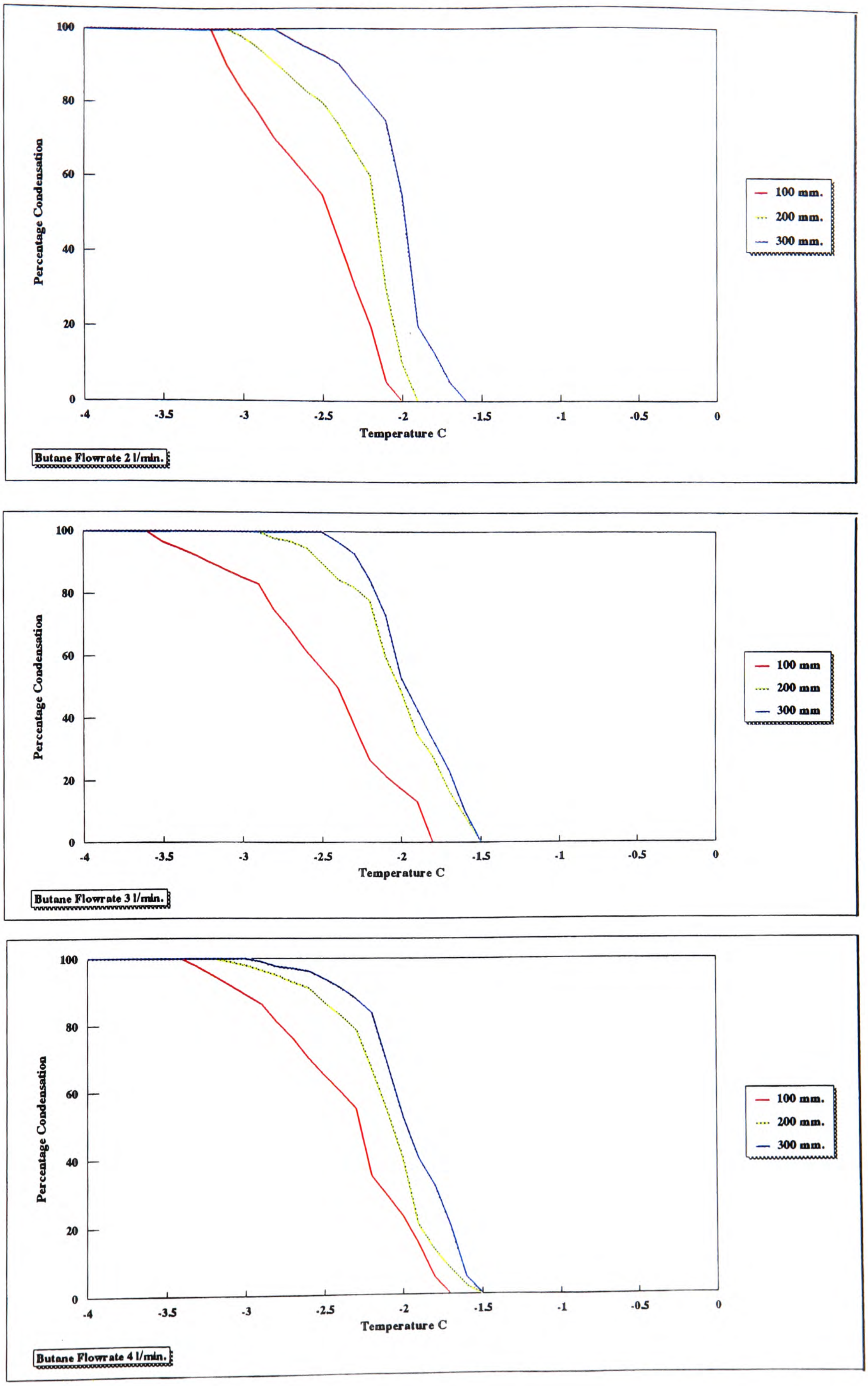


Fig. 48 Effect of Flowrate on Packed Bed Performance : No Packing

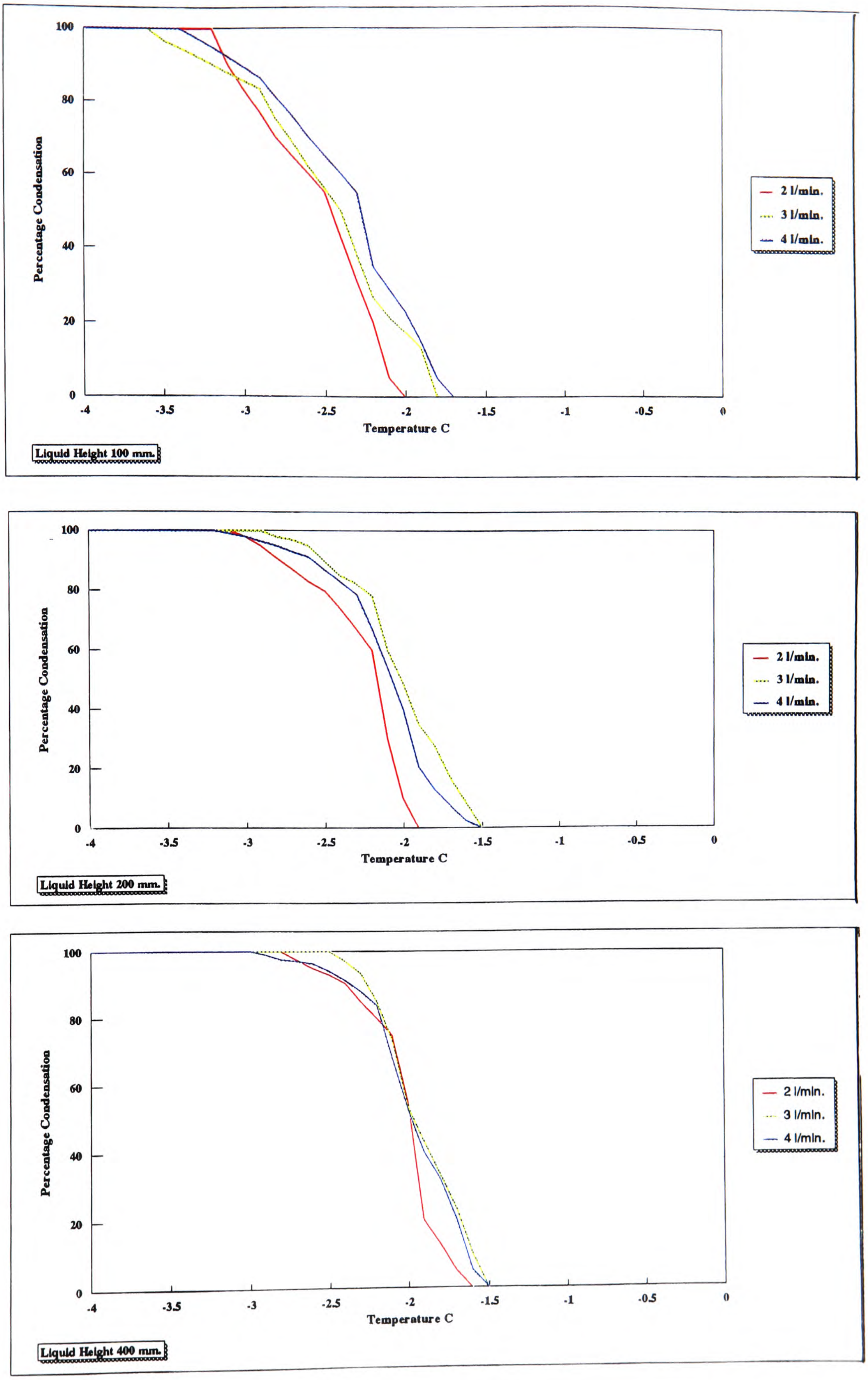
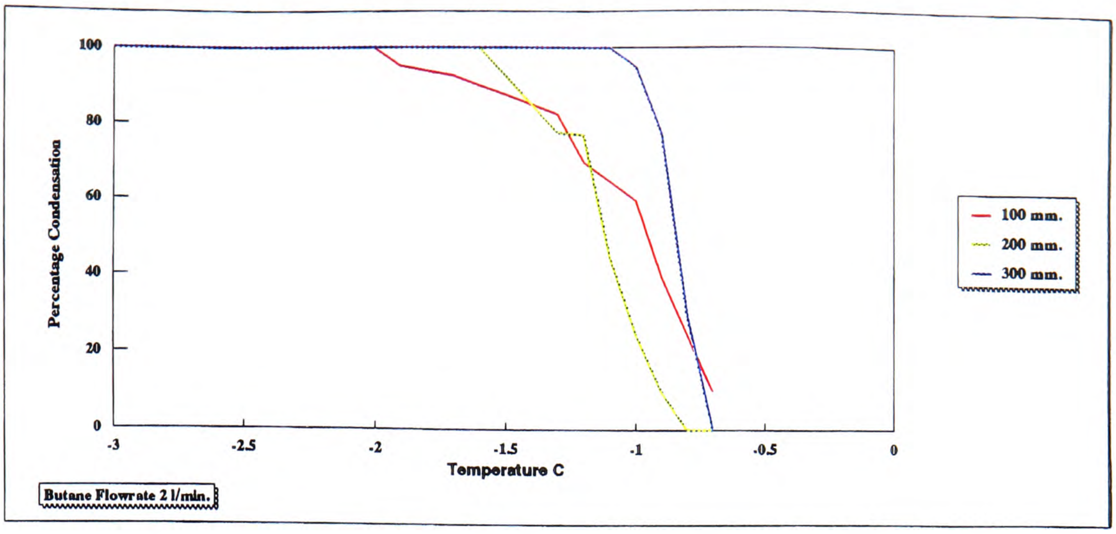
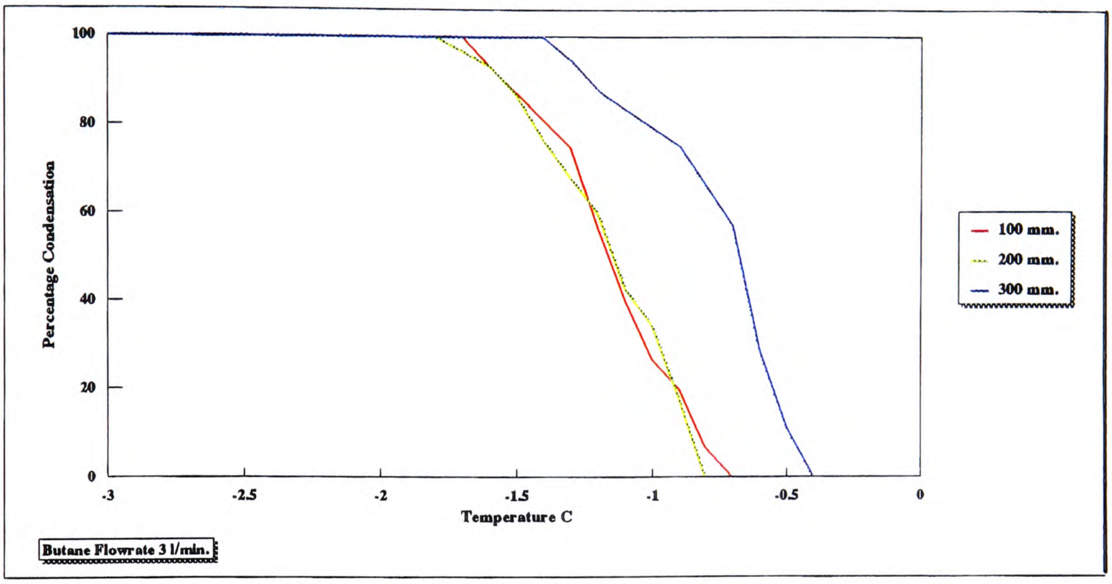


Fig. 49 Effect of Contact Height on Packed Bed Performance : No Packing





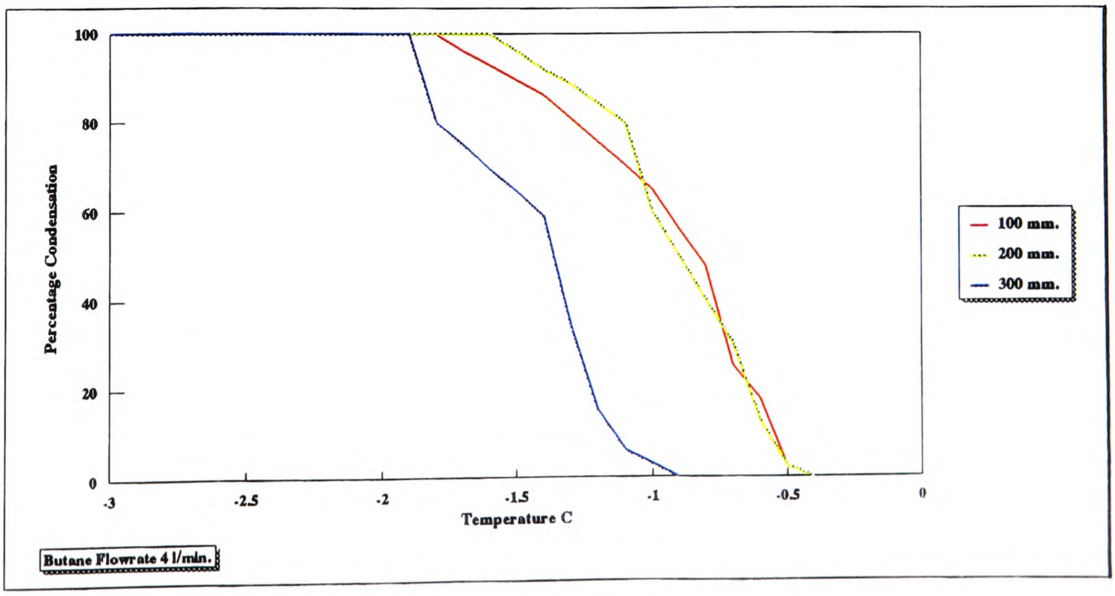


Fig. 50 Effect of Flowrate on Packed Bed Performance : Berl Saddles

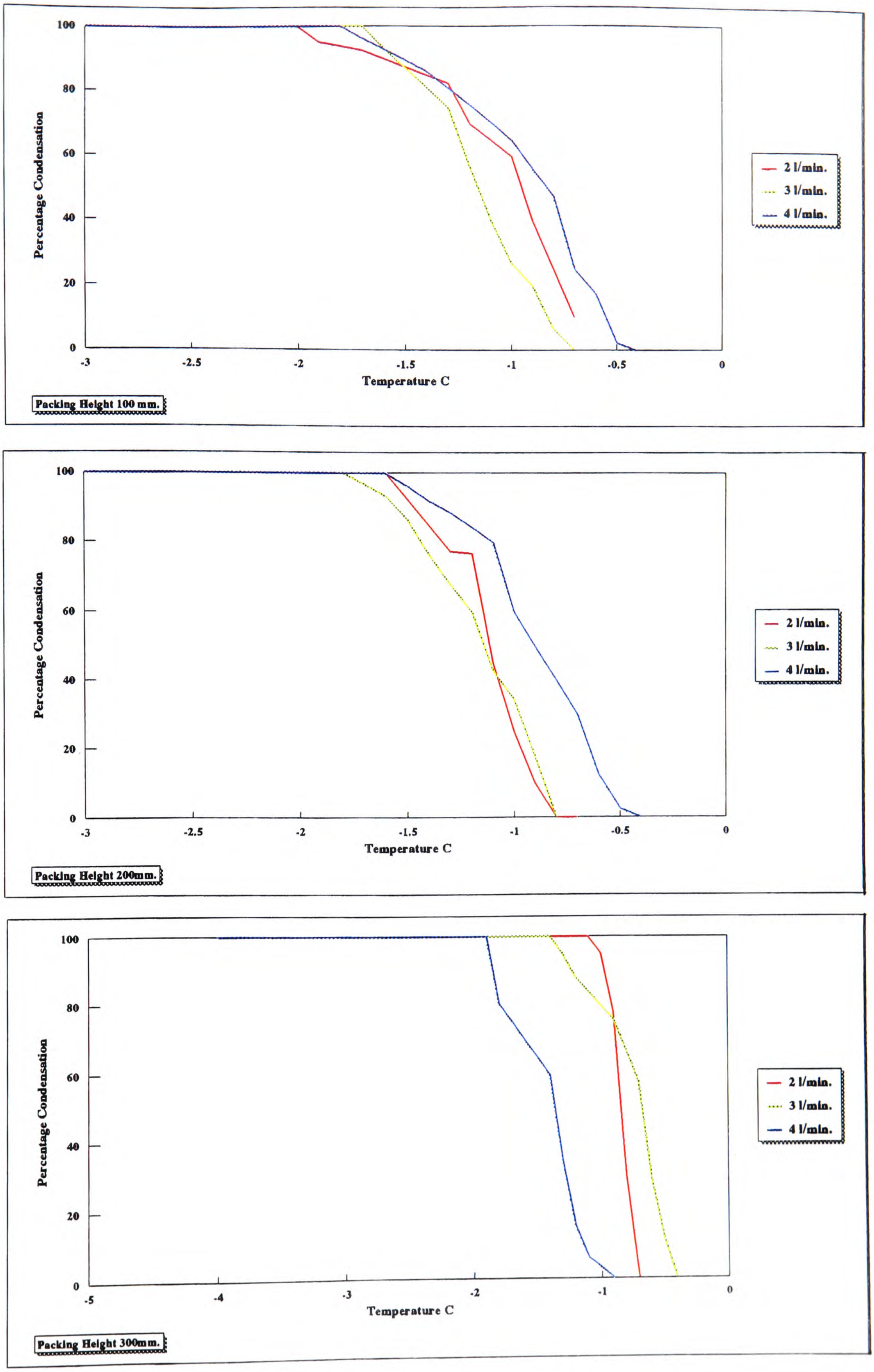


Fig. 51 Effect of Packing Height on Packed Bed Performance : Berl Saddles

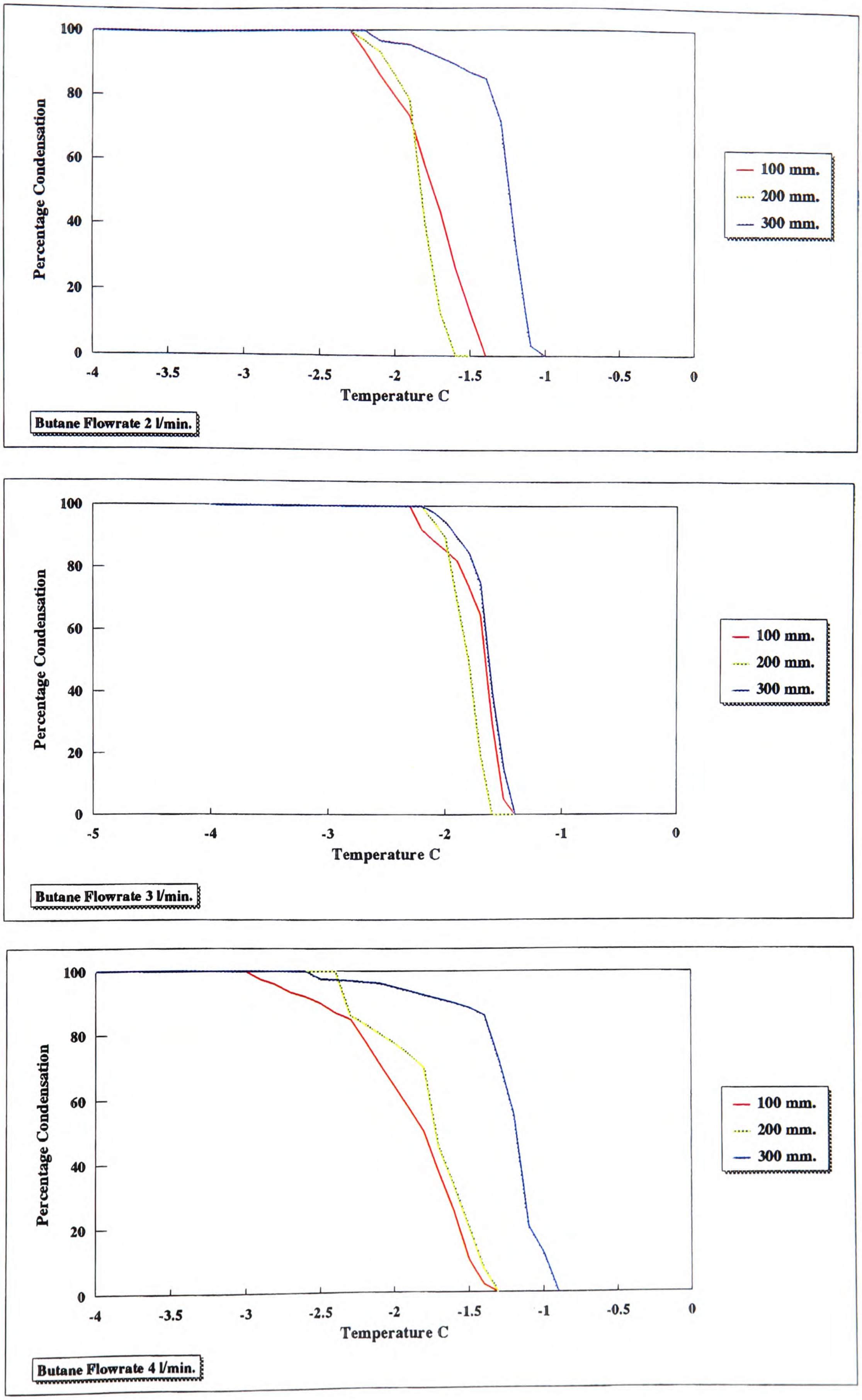


Fig. 52 Effect of Flowrate on Packed Bed Performance : Pall Rings

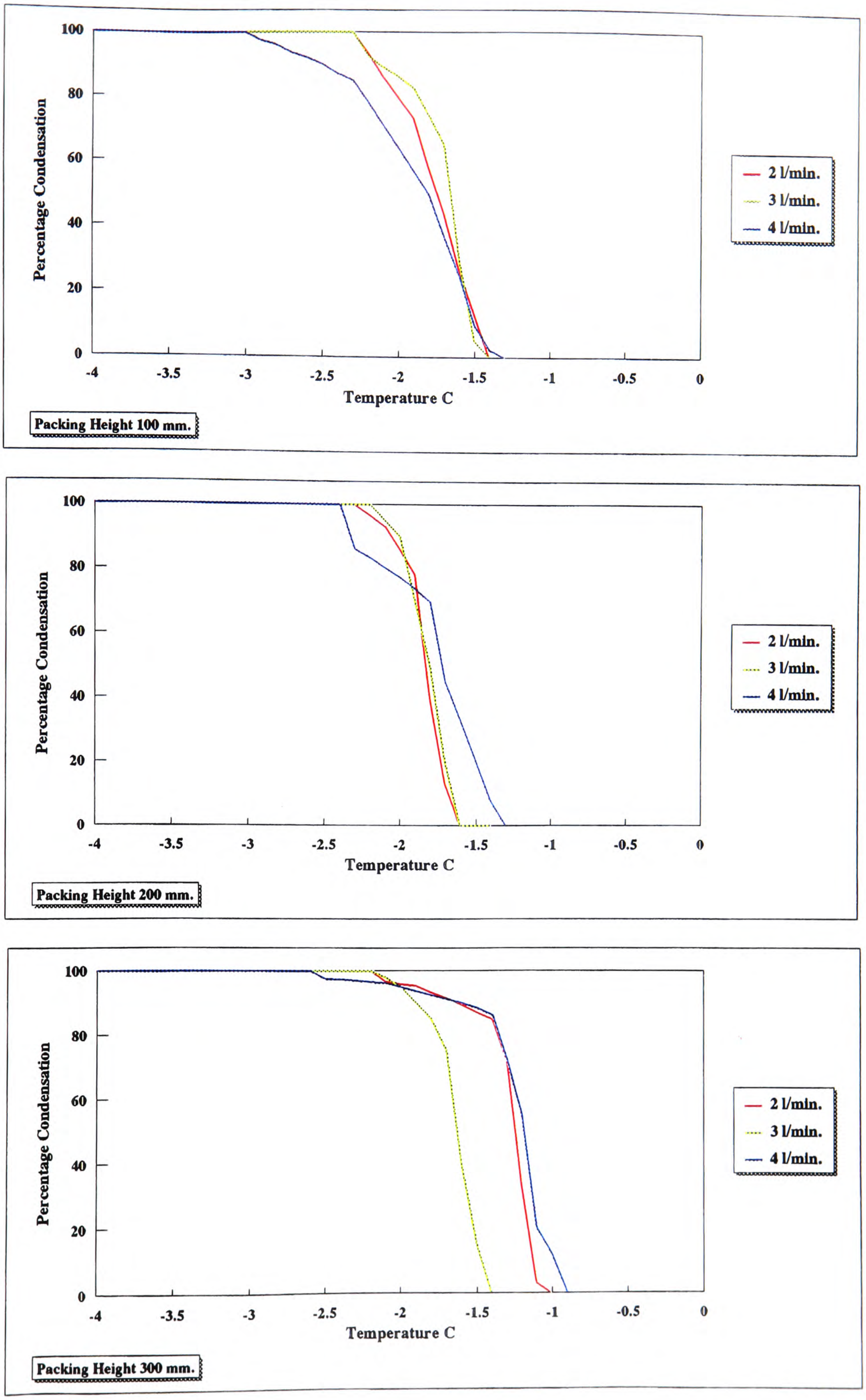


Fig. 53 Effect of Packing Height on Packed Bed Performance: Pall Rings

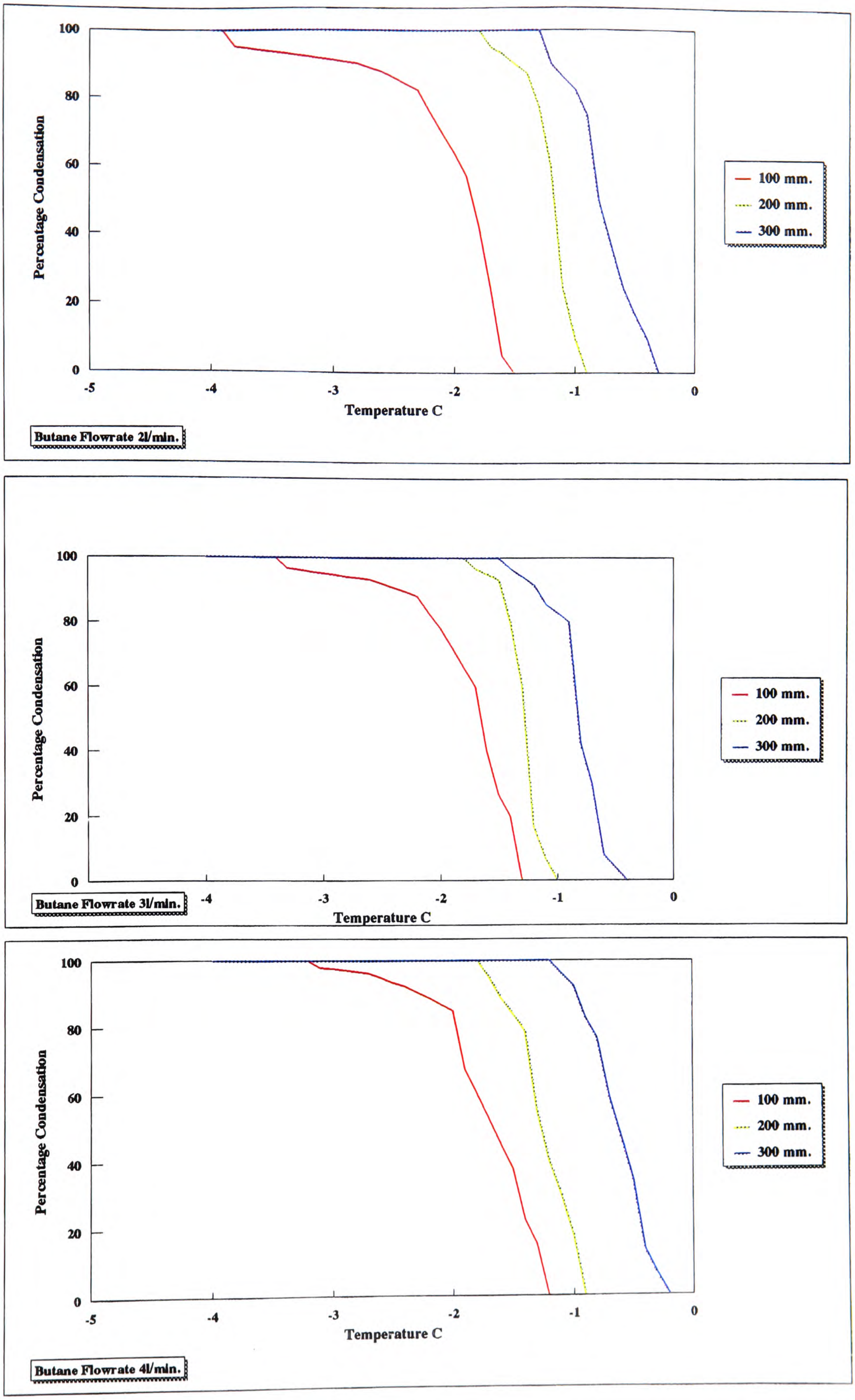


Fig. 54 Effect of Flowrate on Packed Bed Performance : Raschig Rings

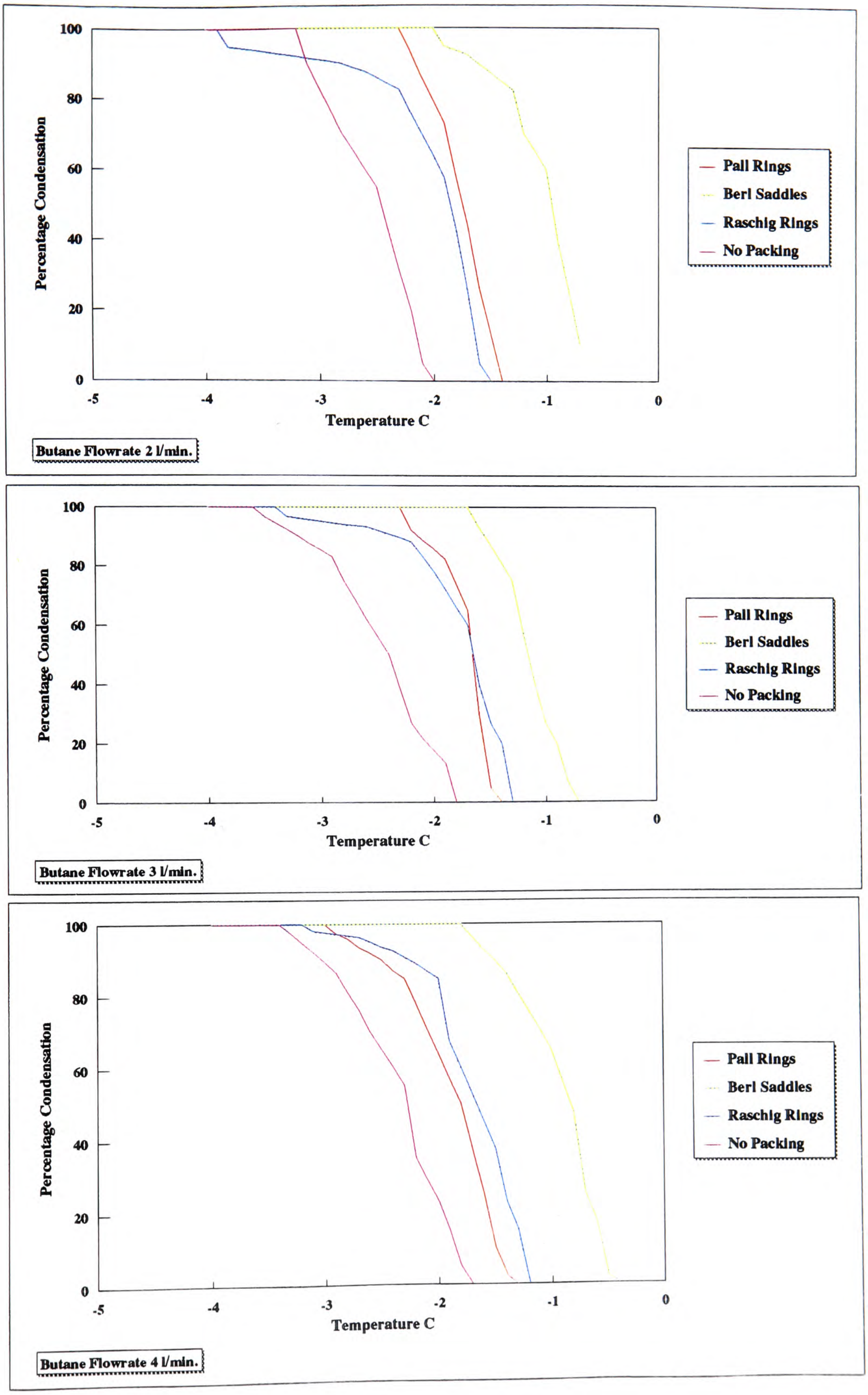


Fig. 56 Effect of Packing Height on Packed Bed Performance :

Bed Height 100 mm.

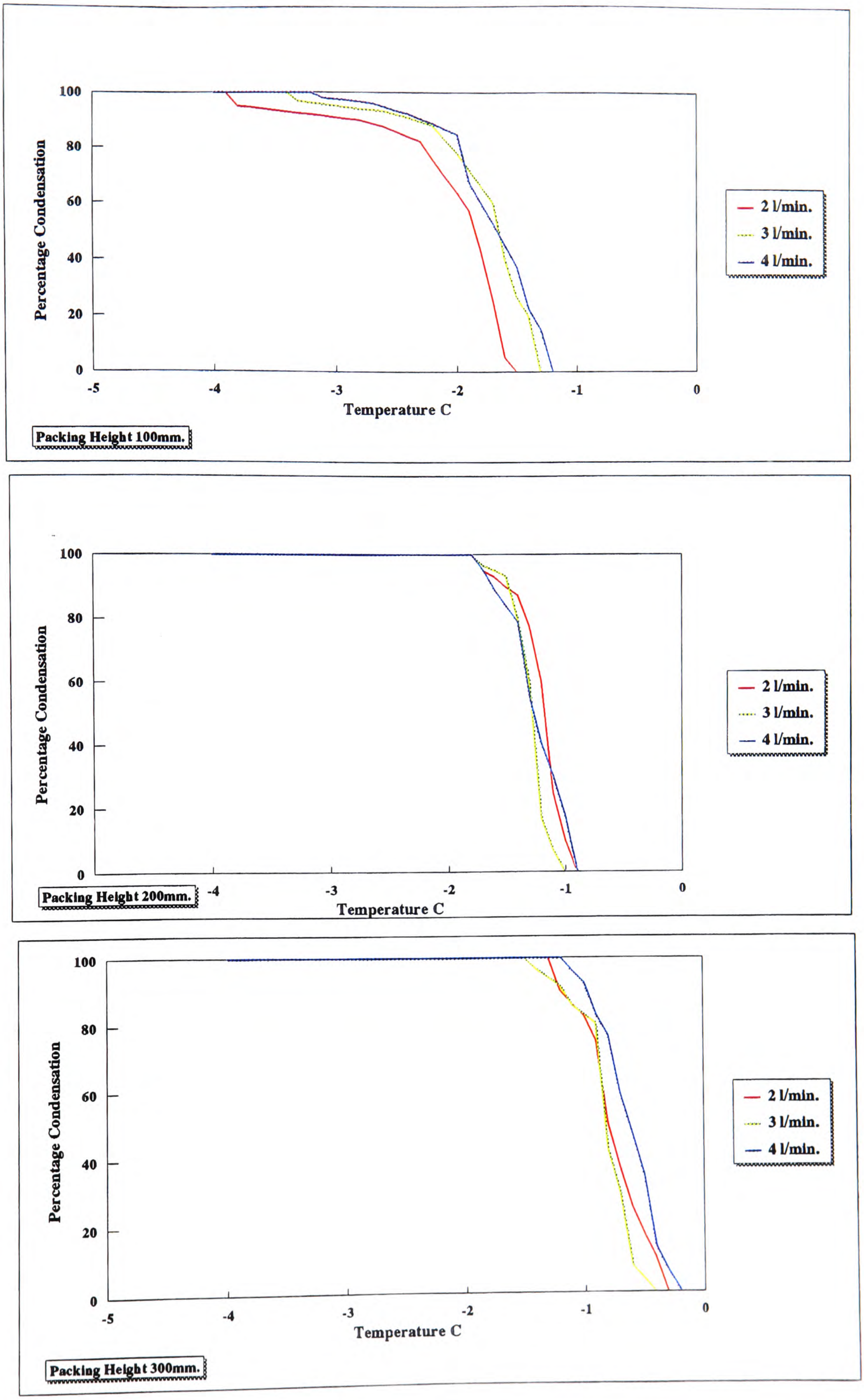
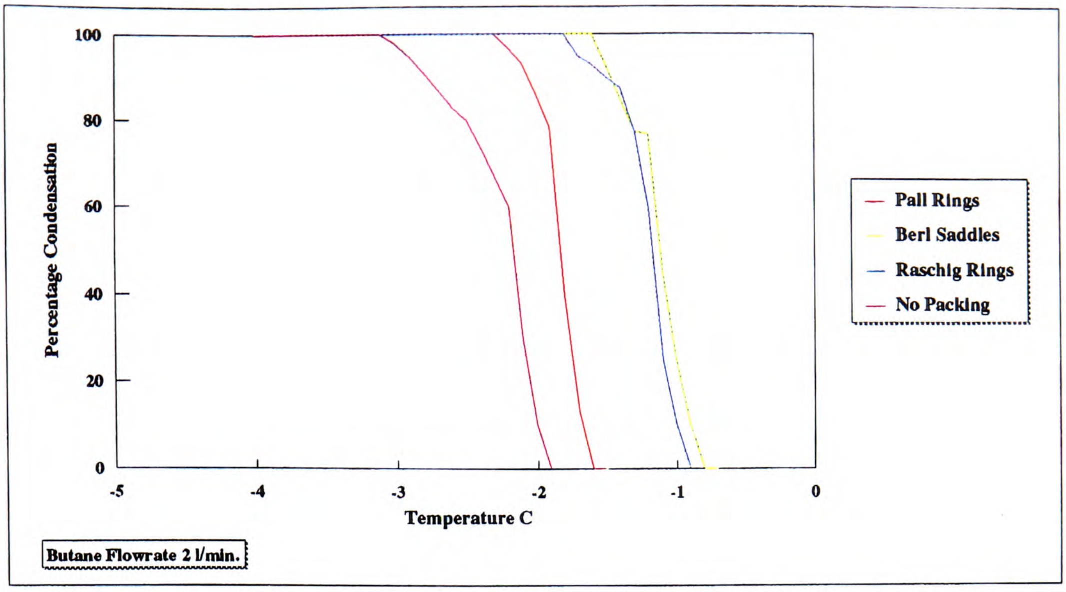
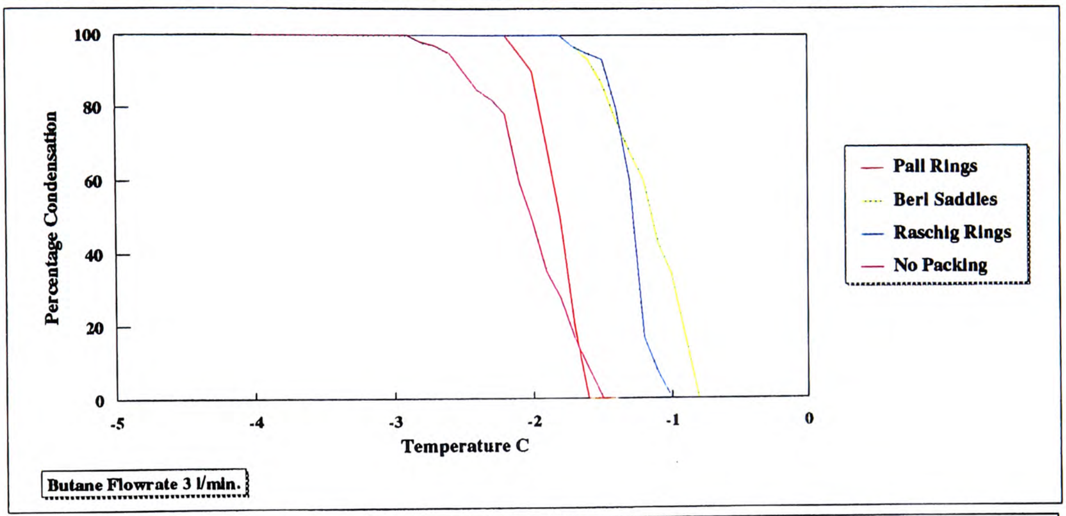


Fig. 55 Effect of Packing Height on Packed Bed Performance : Raschig Rings





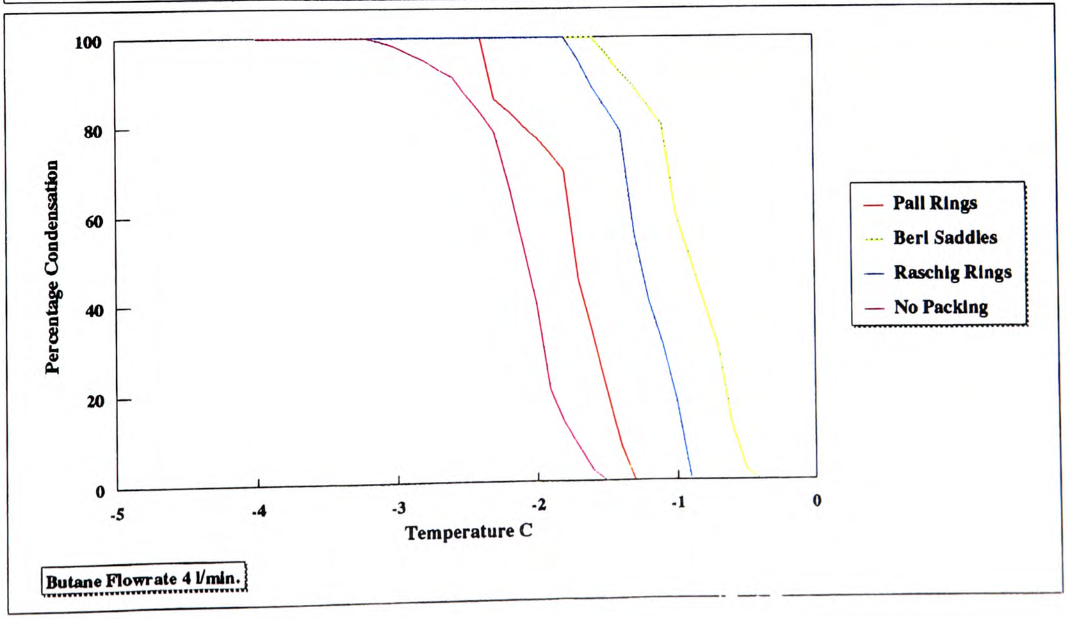


Fig. 57 Effect of Packing Height on Packed Bed Performance:

Bed Height 200 mm.

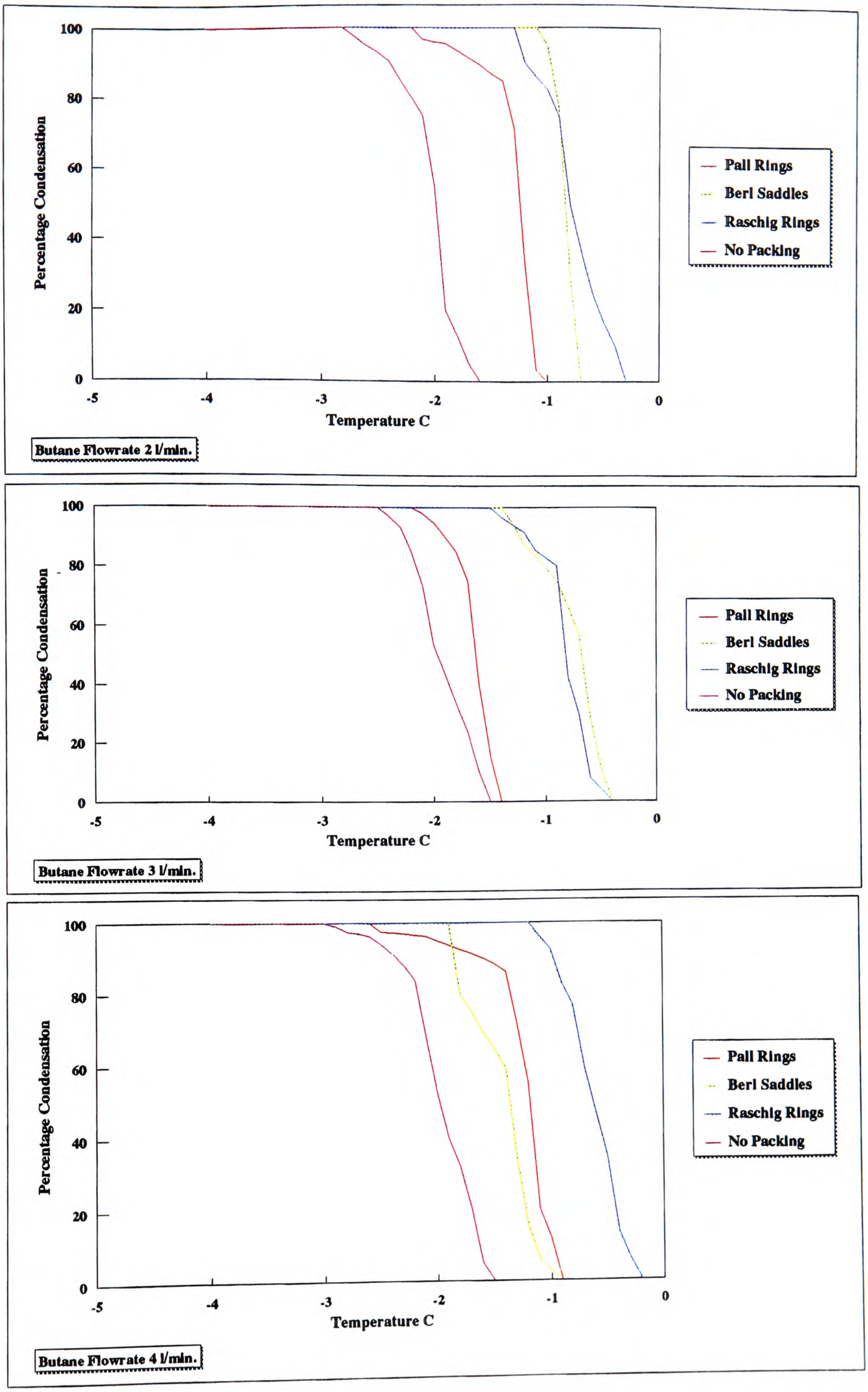


Fig. 58 Effect of Packing Height on Packed Bed Performance:

Bed Height 300 mm.

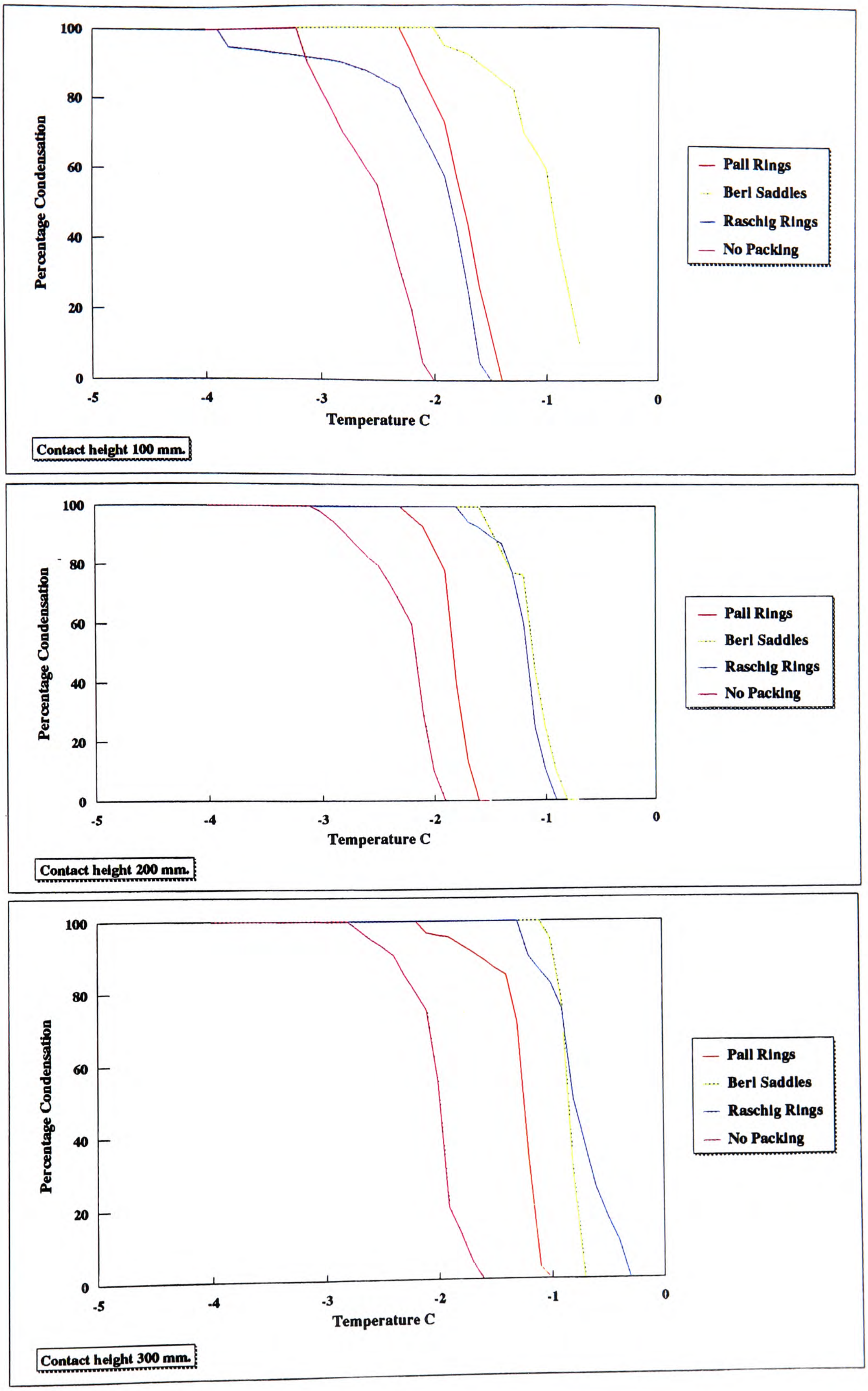


Fig. 59 Effect of Flowrate on Packed Bed Performance :

Butane Flowrate 2 l/min.

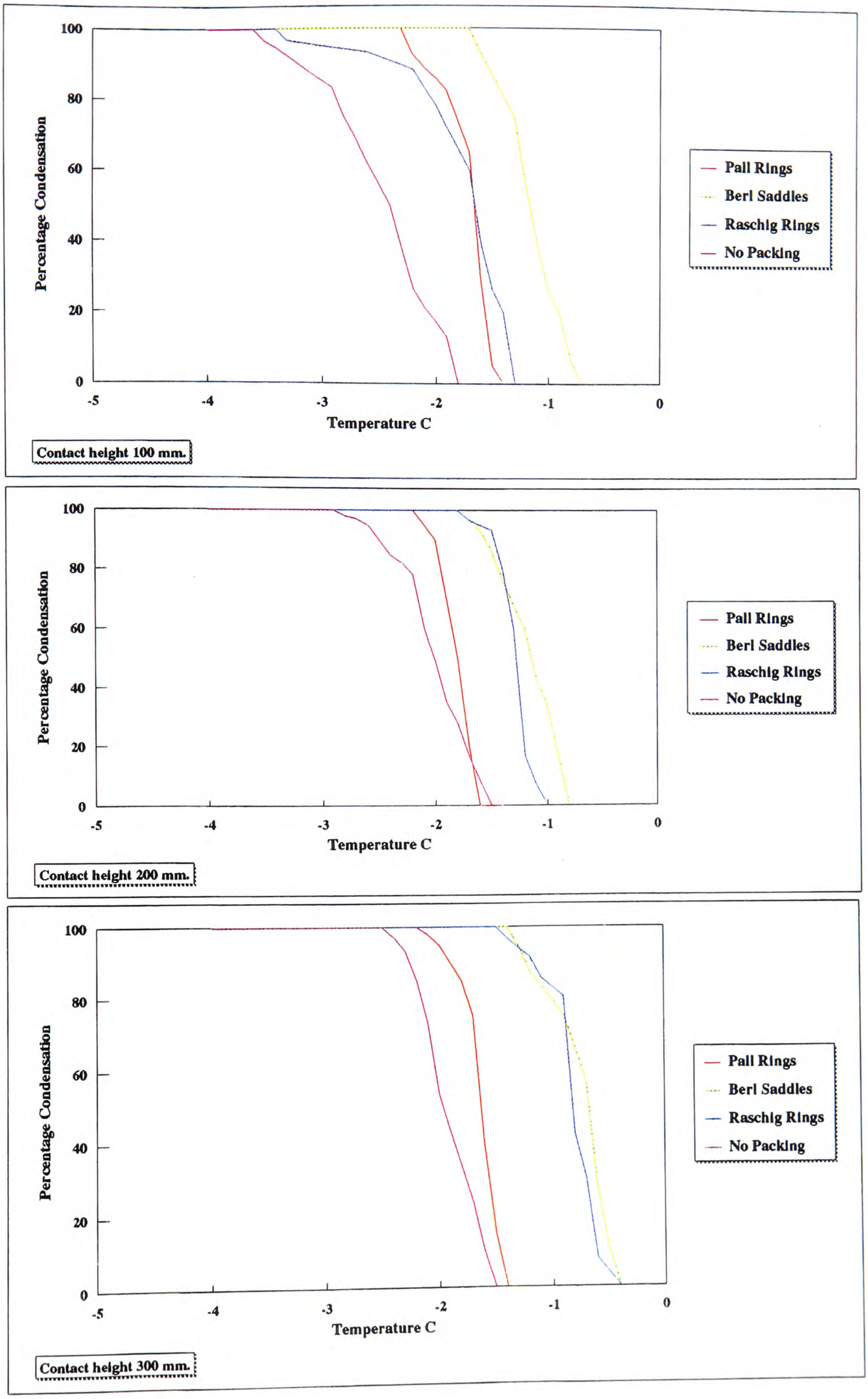
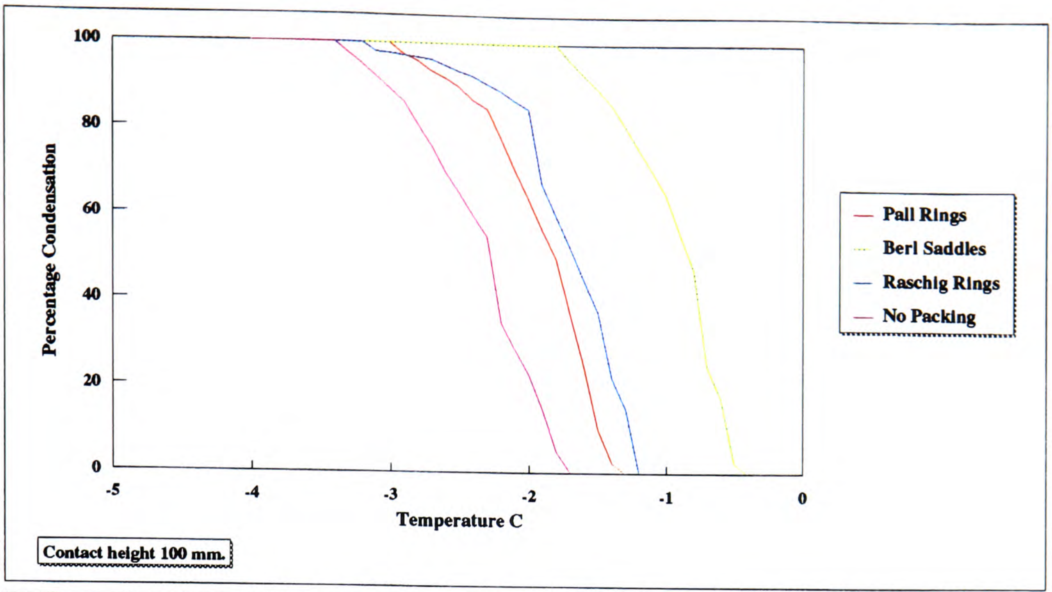
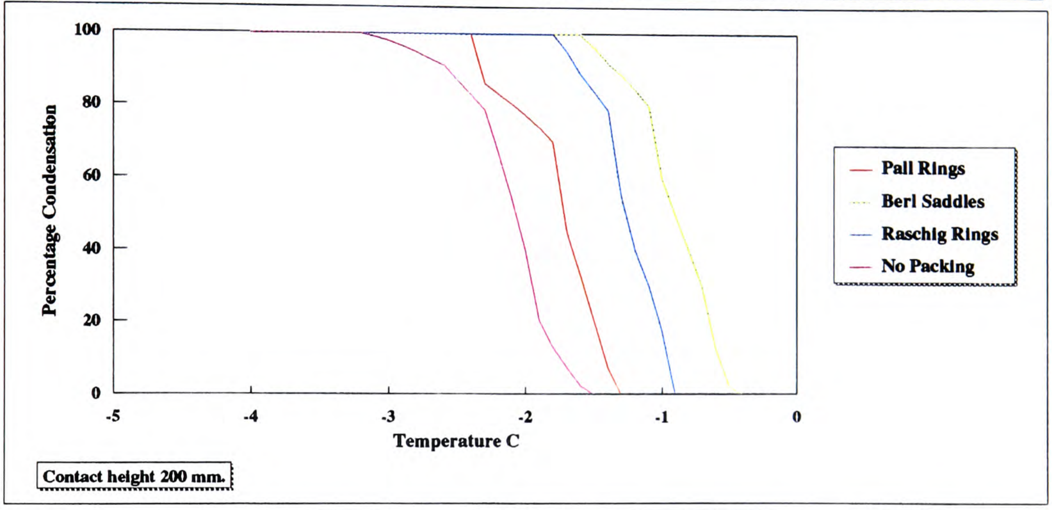


Fig. 60 Effect of Flowrate on Packed Bed Performance :

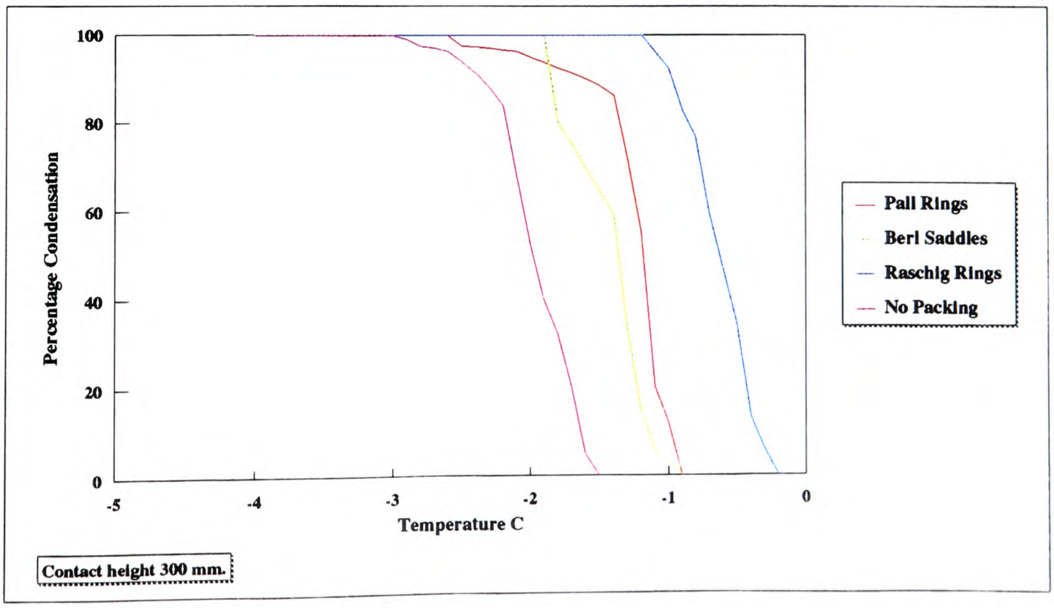
Butane Flowrate 3 l/min.



Contact height 100 mm.



Contact height 200 mm.



Contact height 300 mm.

Fig. 61 Effect of Flowrate on Packed Bed Performance :

Butane Flowrate4 l/min.

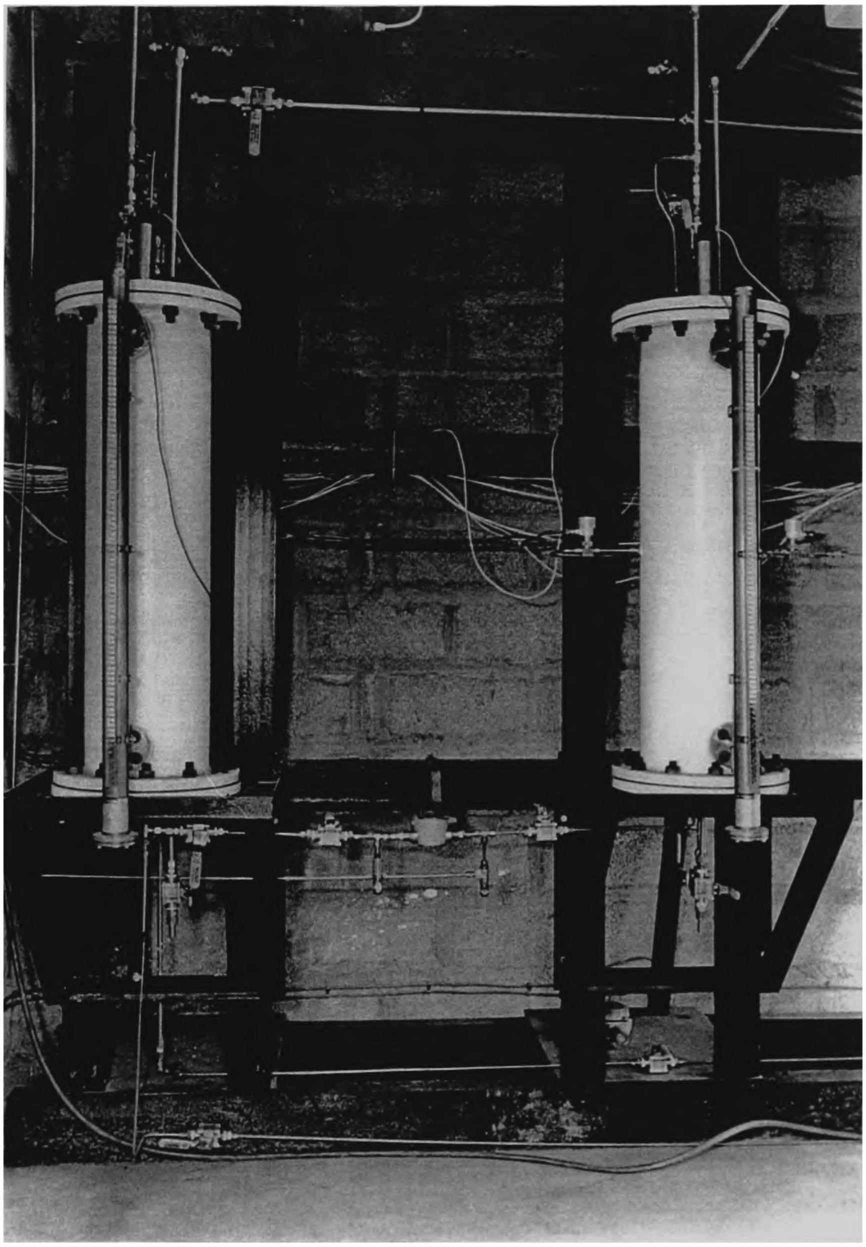


Fig. 62a General View of Pilot Plant : Crystalliser and Flash Vessels

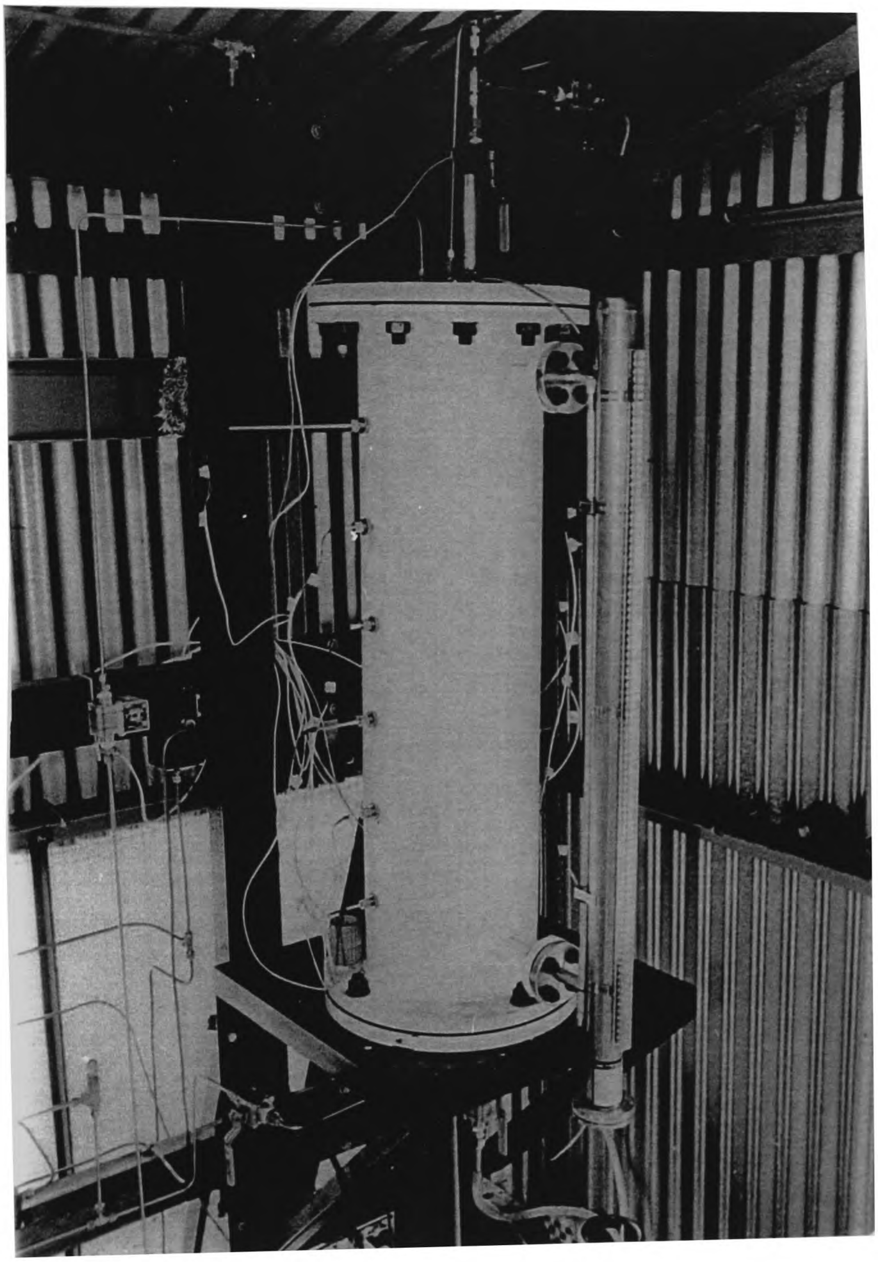


Fig. 62b General View of Pilot Plant : Condenser Vessel

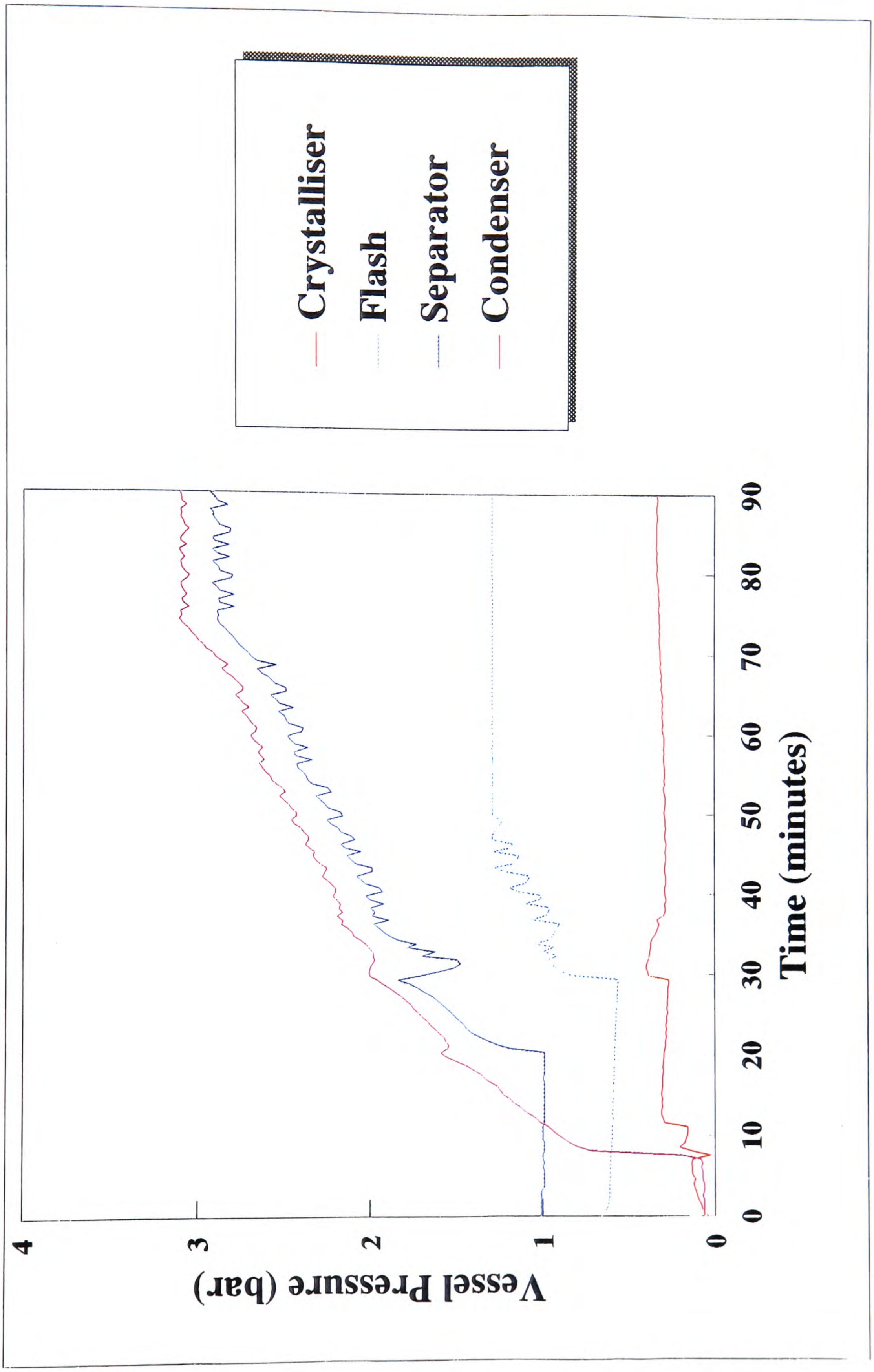


Fig. 63 Pressure Variation During Start - Up

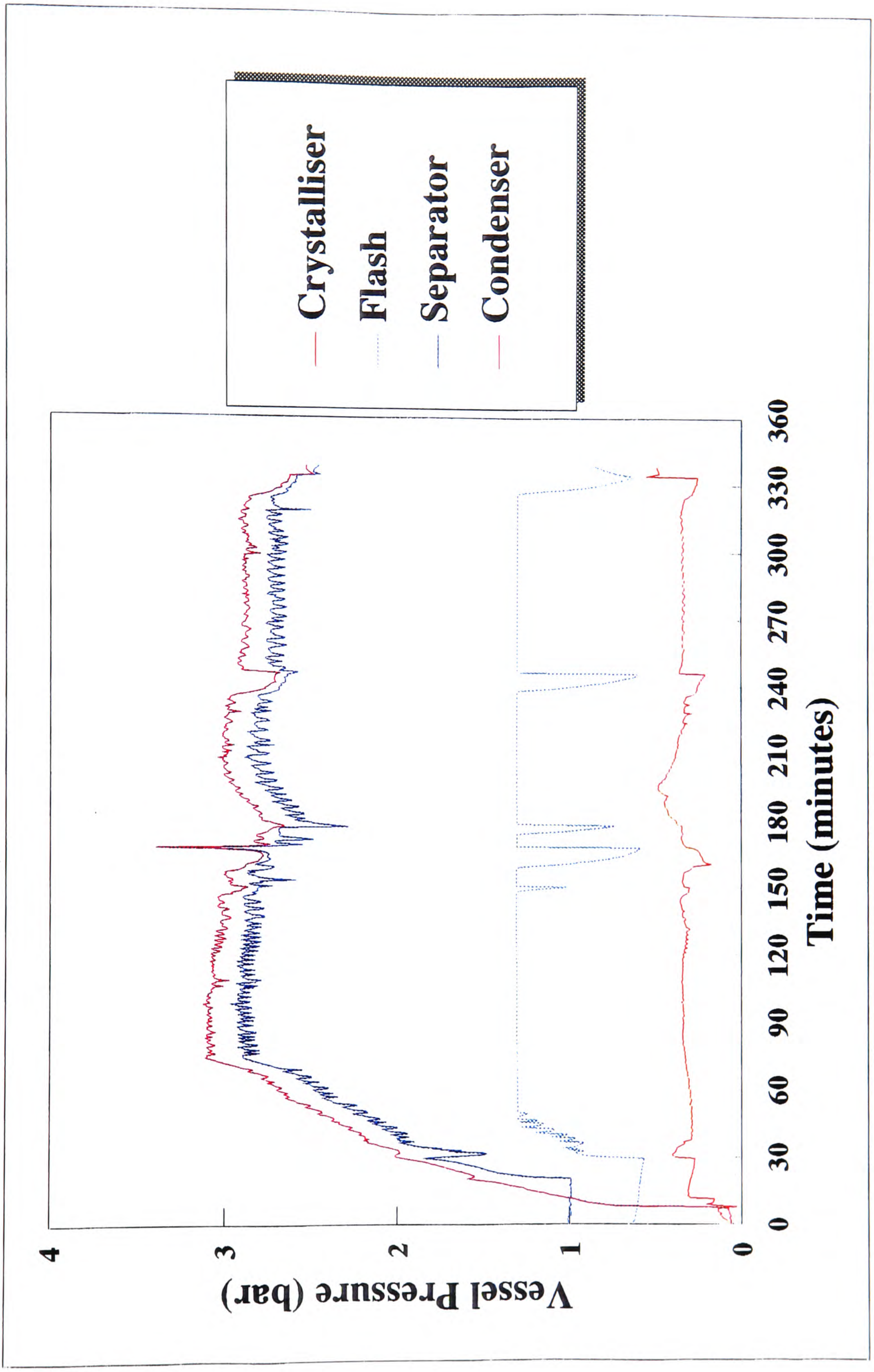


Fig. 64 Normal Operation : Pressures in Water / Butane System

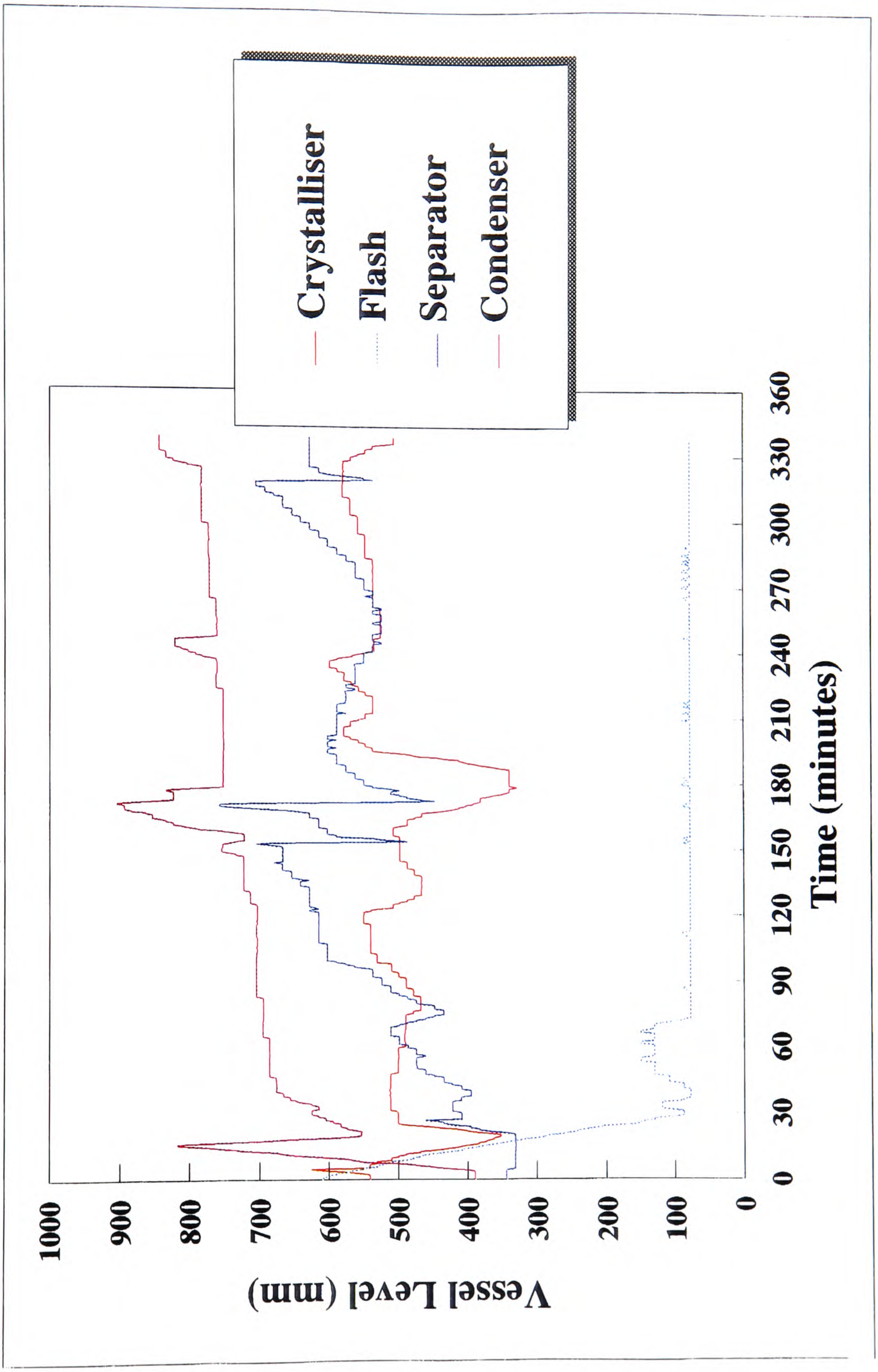


Fig. 65 Normal Operation : Levels in Water / Butane System

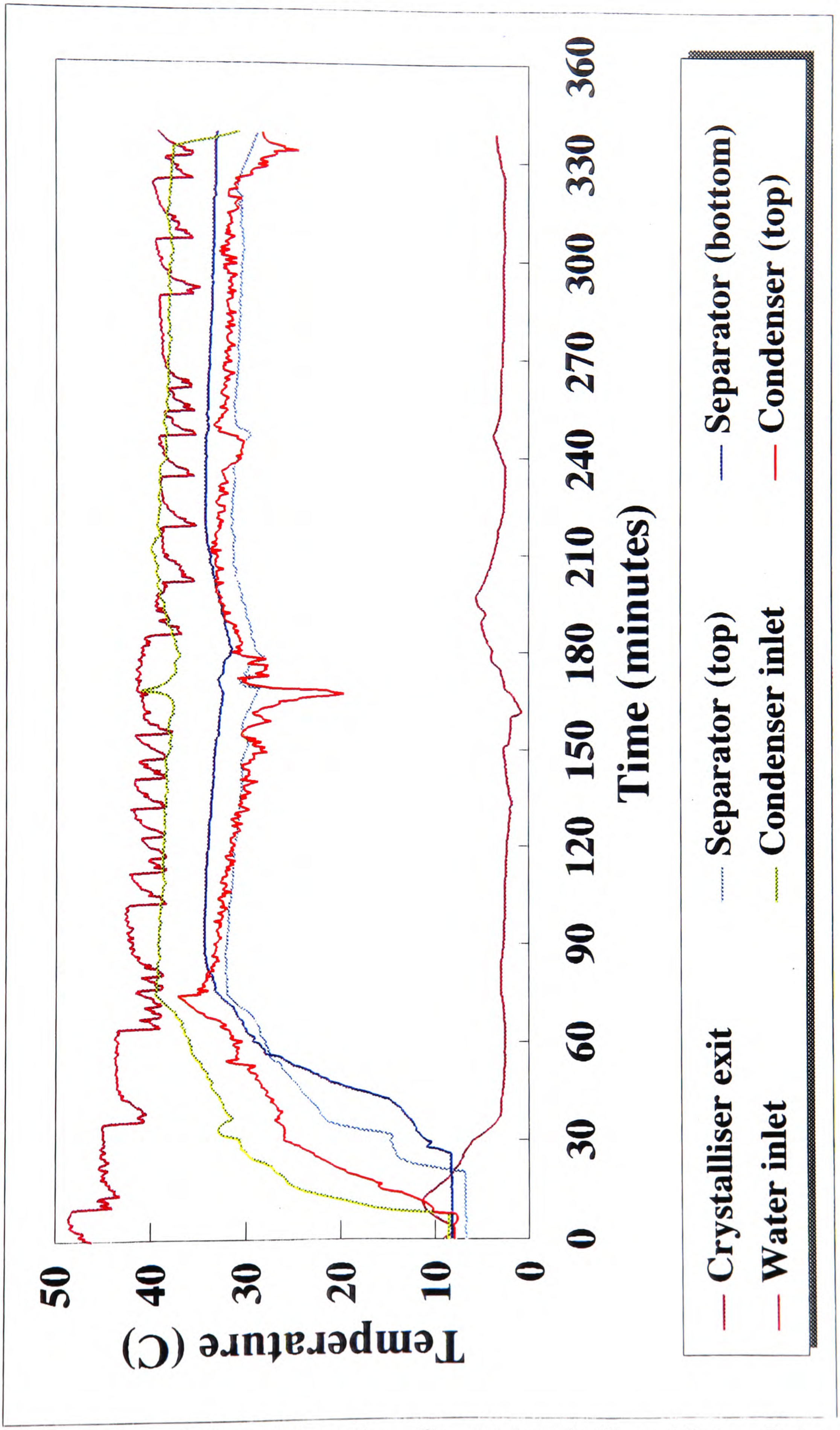


Fig. 66 Normal Operation : Temperatures in Water / Butane System

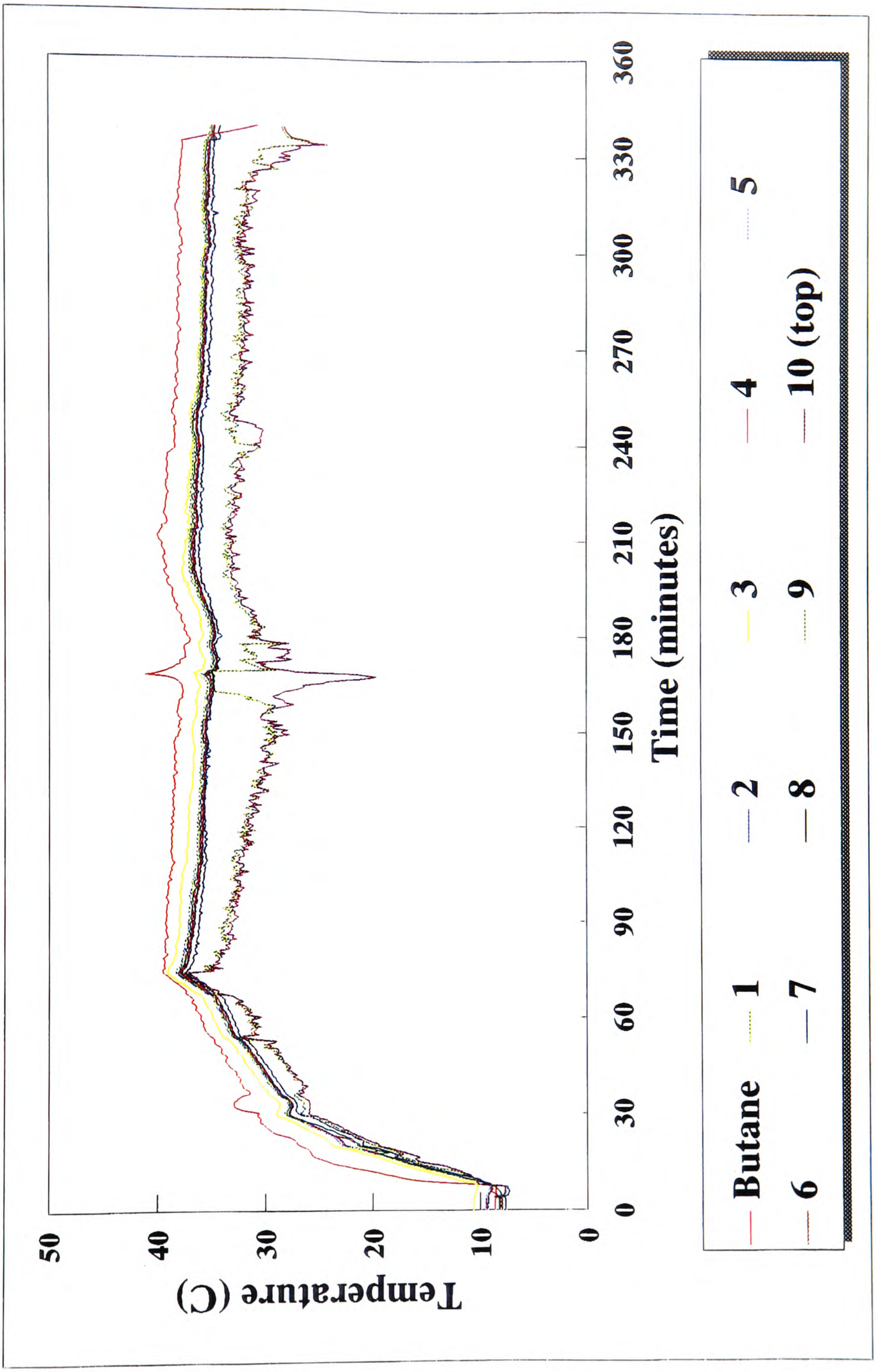


Fig. 67 Normal Operation :

Condenser Temperatures in Water / Butane System

```
SORC  L021108.dat               time   40365    scan   180
PMS,TAM,THW     8.299           9                41.1
flow 1,2        1.419            .831
Ppump 1,2,3     1.209            .033            4.168
VOLTS 1,2,3     2               0                5.5
 0              0               1                0               0

                evap            flash           sep             cond
level            47.8            7.700001        49.8            70.4
press            .336            1.304           2.922           3.101
t-temp                                           32.1            33.3
                                                                 34.1
                                                                 36.4
                                                                 37.2
                                                                 36.9
                                                                 37.4
                                                                 37.1
                                                                 38.2
                                                                 36.9
                                                                 37.4
b-temp           2.9                             34.2            39.3
```

```
SORC  L021108.dat               time   51224    scan   540
PMS,TAM,THW     7.815            9.600001        38
flow 1,2        1.516            1.98
Ppump 1,2,3     1.179            .018            4.599
VOLTS 1,2,3     2                0               6
 0              0                1               0               0

                evap            flash           sep             cond
level            53.7            8.8             53.7            77.2
press            .322            1.308           2.722           2.846
t-temp                                           30.8            31.1
                                                                 31.7
                                                                 35.1
                                                                 35.9
                                                                 35.6
                                                                 36.1
                                                                 35.7
                                                                 36.1
                                                                 35.5
                                                                 35.9
b-temp           2.9                             33.9            38.1
```

Fig. 68 Normal Operation : Typical VDU Displays

```
sorc stats of data file      L021108.dat


number of data sets           680

mnenonic        mean          max            min

    tim          45173.41      55633          32259
    pms          7.93          8.477999       -.127
    tam          9.29          10.6            7.3
    thw          40.28         53.8            34.7

    fl1          1.5           2.502          -.002
    tf1          .22           1               0
    fl2          1.39          2.29           -.001
    tf2          0             0               0

    pp1          1.39          3.908          -.017
    pp2          .02           .049            .003
    pp3          4.03          5.946          -.032
    vp1          2.19          5               0
    vp2          0             0               0
    vp3          5.3           7.5             0

    lwe          50.61         86.2            4
    lbf          11.72         60.9            7.6
    lbs          54.62         75.7            33
    lbc          72.13         90.4            6.8

    pte          .31           .55            -.004
    ptf          1.17          1.31            .563
    pts          2.52          3.33            .952
    ptc          2.65          3.391           .052

    tts          27.66         32.2            6
    tbe          3.49          11.3            .7
    tbs          29.47         34.4            8.100001
    tbi          35.78         41.1            7.5
    t9c          29.23         37.1            6.7
    t8c          29.97         37.6            6.7
    t7c          32.58         37.4            6.3
    t6c          33.24         38.1            6.9
    t5c          33.01         37.8            6.8
    t4c          33.55         38.3            6.9
    t3c          33.17         37.9            6.7
    t2c          34.08         39.1            8
    t1c          33.04         37.7            6.7
    t0c          33.46         38.2            6.7
```

Fig. 69 Normal Operation : Statistical Analysis of Test

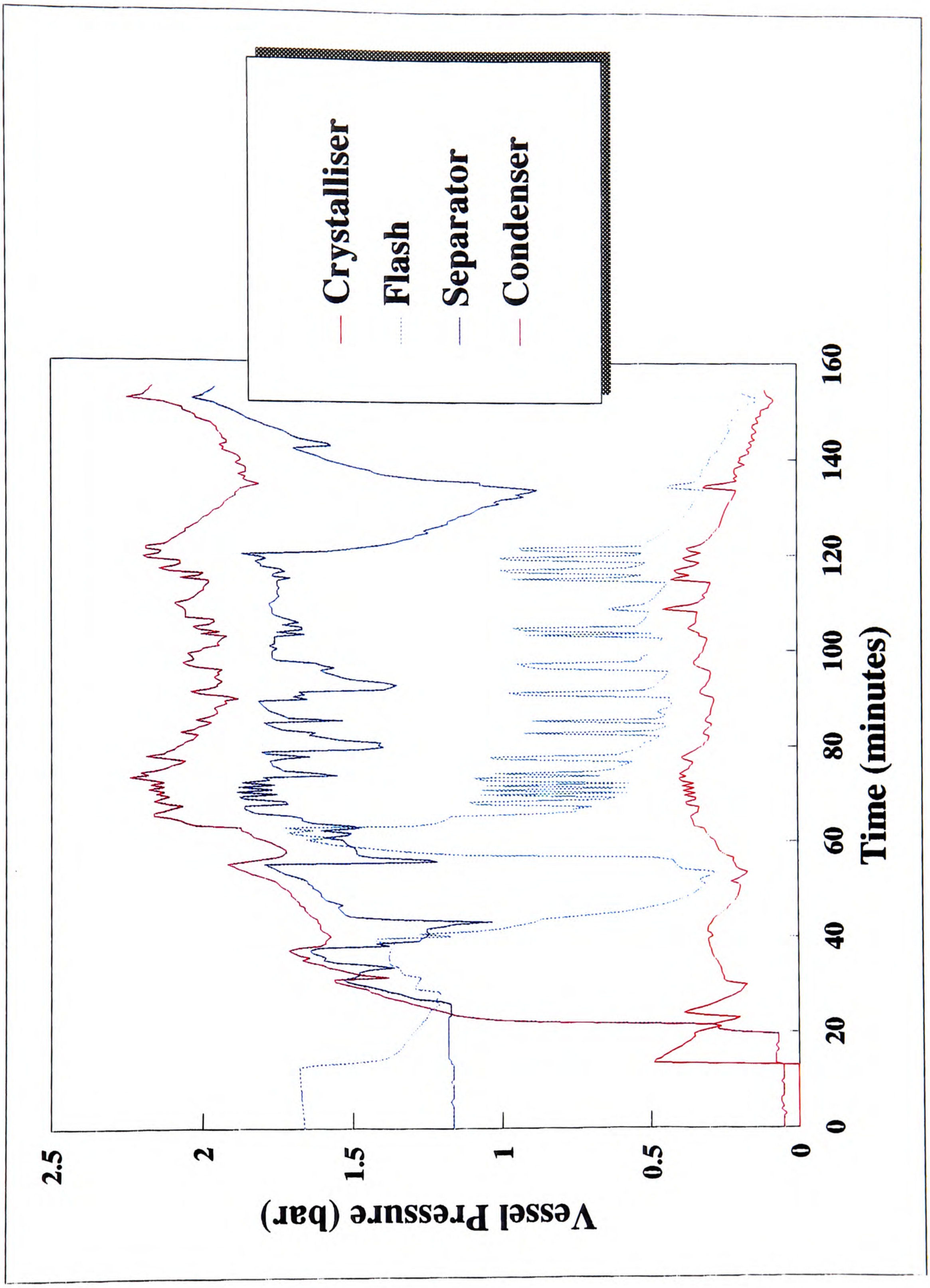


Fig. 70 Reduced Compressor Output :

Pressures in Water / Butane System

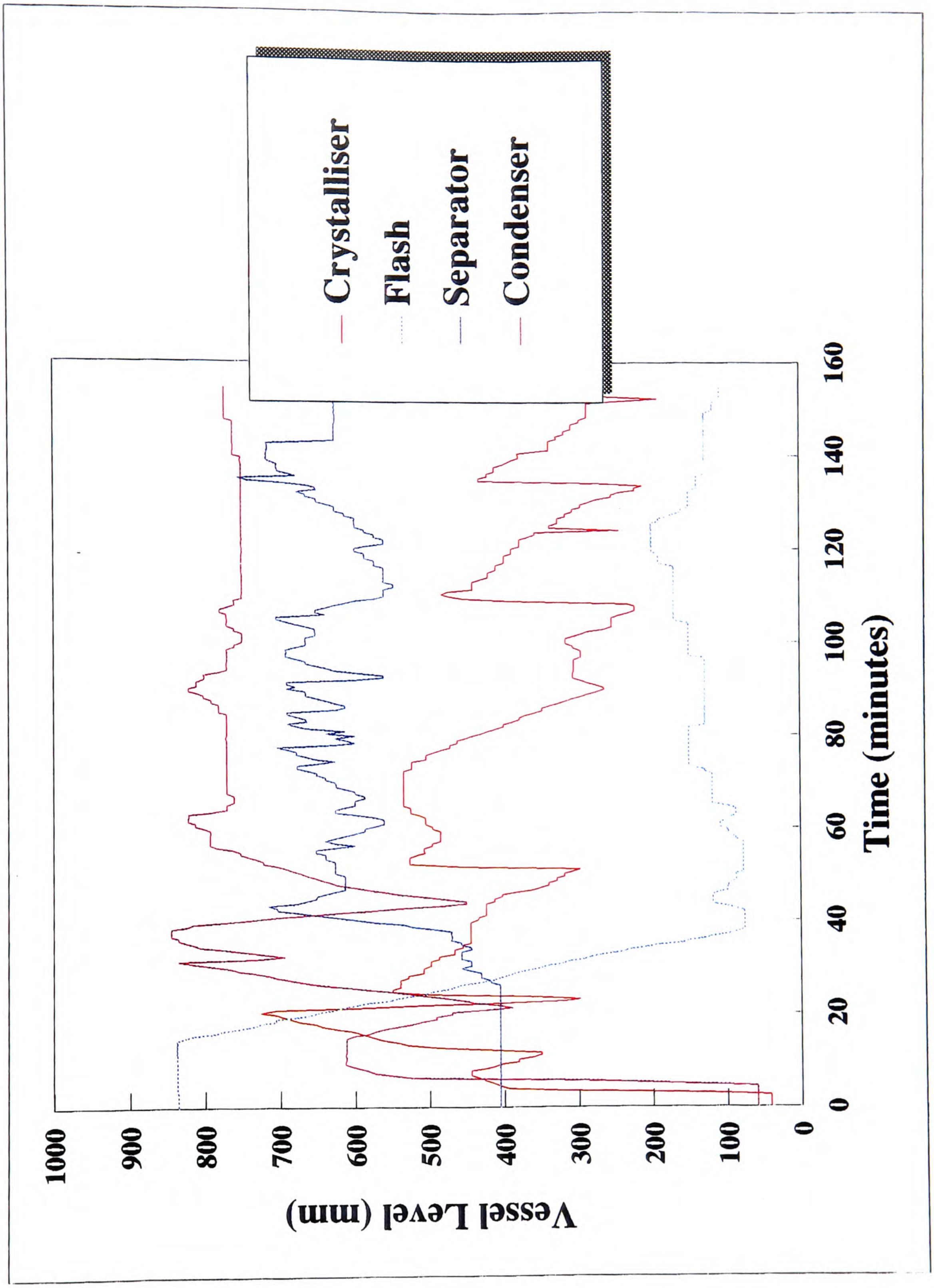


Fig. 71 Reduced Compressor Output :

Levels in Water / Butane System

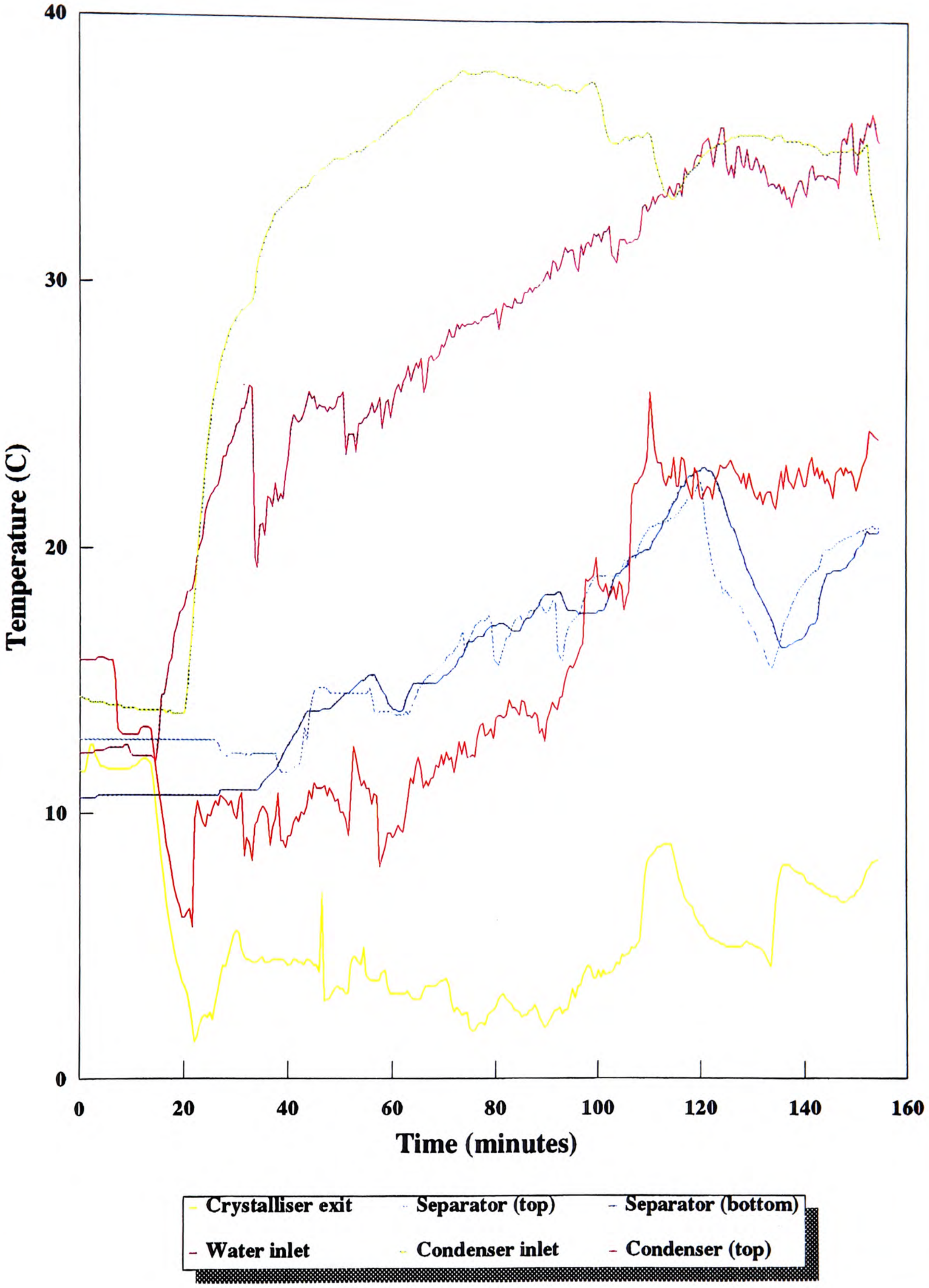


Fig. 72 Reduced Compressor Output :

Temperatures in Water / Butane System

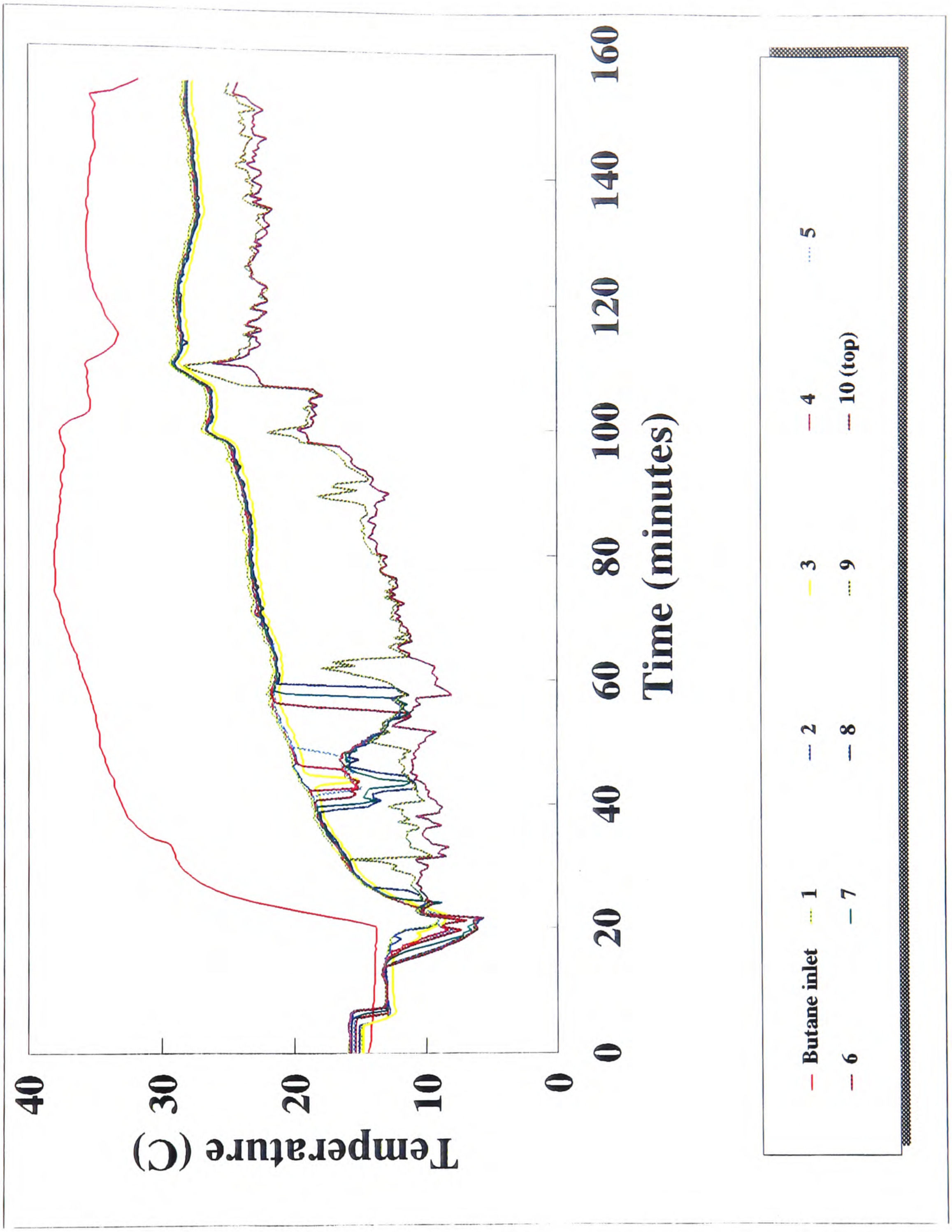


Fig. 73 Reduced Compressor Output :

Condenser Temperatures in Water / Butane System

```
sorc stats of data file      L111513.dat


number of data sets           306

mnenonic         mean           max            min

     tim          54858.49       59523          50237
     pms          7.33           8.001001       6.684
     tam          13.05          14.5           11.5
     thw          27.32          36.5           12

     fl1          1.73           2.19          -8.999999E-03
     tf1          0              0              0
     fl2          1.48           2.881         -.007
     tf2          0              0              0

     pp1          4.37           4.77           .022
     pp2          7.45           9.8            .078
     pp3          4.31           5.574         -.005
     vp1          8.05           10             0
     vp2          6.9            9              0
     vp3          5.54           7              0

     lwe          39.9           72.6           4.1
     lbf          24.66          83.8           7.6
     lbs          58.03          75.6           40.5
     lbc          70.17          84.5           6

     pte          .25            .489          -.077
     ptf          .8             1.729          .129
     pts          1.51           2.033          .88
     ptc          1.63           2.249          .043

     tts          16.23          22.7           11.6
     tbe          4.15           12.6          -1.7
     tbs          15.92          23.2           10.6
     tbi          31.89          38.1           13.8
     t9c          15.52          26.1           5.7
     t8c          16.5           28.3           5.8
     t7c          21             29.1           5.6
     t6c          21.29          29.3           5.6
     t5c          21.61          29.3           6.9
     t4c          21.9           29.2           7.9
     t3c          22.06          29.3           8.3
     t2c          21.63          28.8           8.399999
     t1c          22.15          29.2           9
     t0c          22.42          29.5           9
```

Fig. 74 Reduced Compressor Output : Statistical Analysis of Test

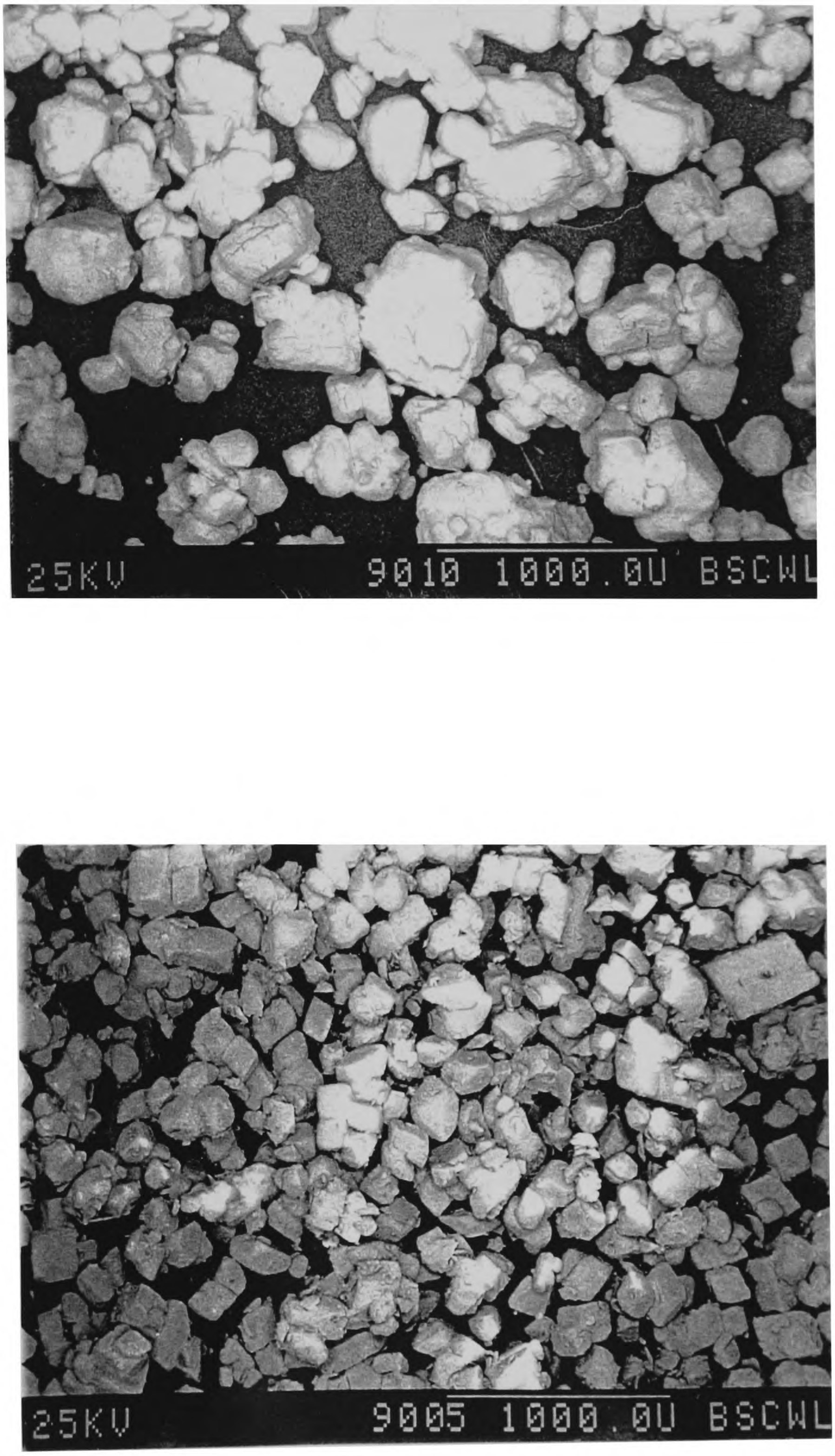


Fig. 75 Iron (2) Sulphate Crystals Produced from Aqueous Solution

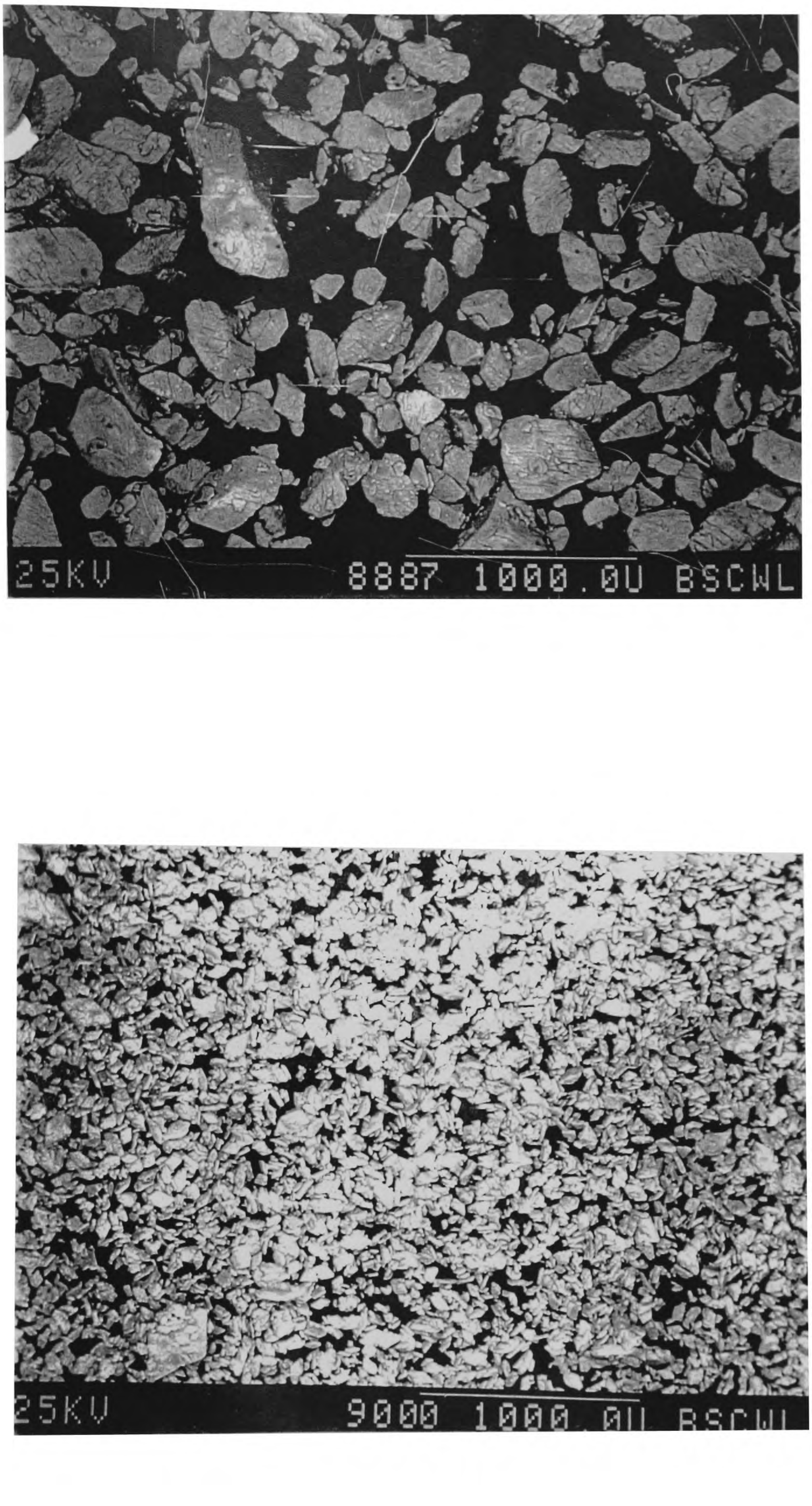


Fig. 76 Copper (2) Sulphate Crystals Produced from Aqueous Solution

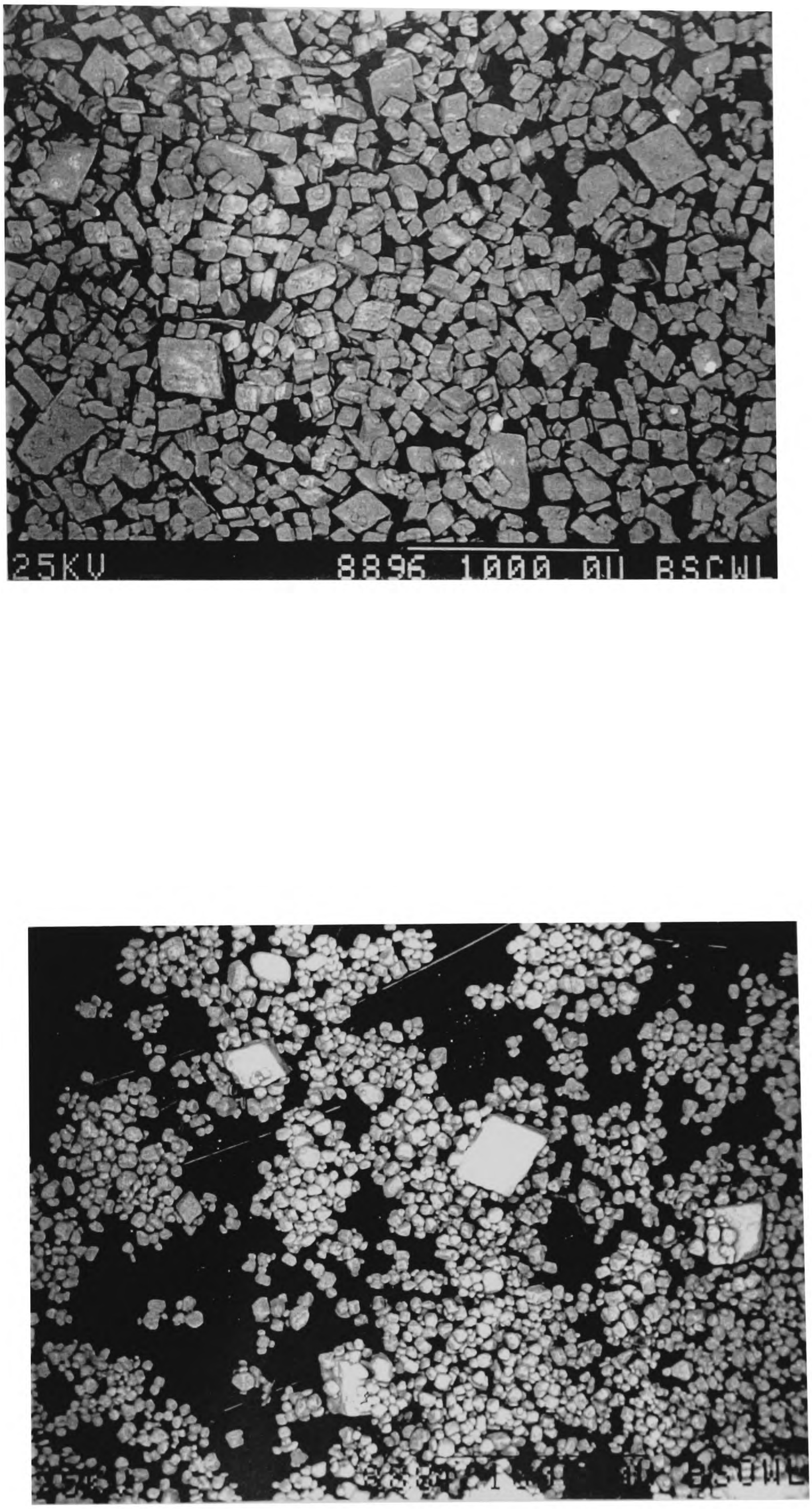


Fig. 77 Iron (2) Sulphate Crystals Produced from Waste Pickle Liquor