

Planing and Operation of a Plant for the Crystallization
of Adipic Acid

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1. Use of Adipic Acid

With the invention of the polyamide nylon by W. H. Carothers in the early 30s a new era of synthetic textile fibers began. Basic material for the newly discovered nylon 6,6 was adipic acid which up to this time was not much used in the chemical industry. From then the importance of adipic acid has grown rapidly. Up to now this material is mainly used for the manufacturing of polyamides.


In order to understand the difficulties in the preparation of adipic acid there has to be a description of the reaction steps.

2. Process for the Production of Adipic Acid

2.1 Synthese

Crude material are mainly cyclohexanol and cyclohexanone which are made from cyclohexane.


One of the best processes as well as from the technical and from the economical side is the oxidation of a mixture of both of these substances with nitric acid.

Cyclohexanol and cyclohexanone are oxidized with nitric acid. The resulting nitrous acid forms with cyclohexanone α -nitrosoketone which again will be oxidized by the nitric acid to α -nitrocyclohexanone. A small part of it is transformed into aromatic nitro compounds. The main quantity of the nitrocyclohexanone and the nitrosyl cation form the α -nitronitrosocyclohexanone which hydrolyses to "nitrolic acid". This nitrolic acid finally decomposes into nitrous oxide and adipic acid. During the described twofold nitrosation of the cyclohexanone glutaric and succinic acid are produced as by products. 

In practice the reaction takes places at temperatures at about 50 - 80° C and 1 bar. Ammoniummetavanadate and coppernitrate are used as catalyts. The process yield reaches 93 - 96 %.

2.2 Preparation

2.2.1 Principle of process

As mentioned before besides adipic- and nitric acid the reaction liquor contains some amounts of aromatic nitro compounds (as pictric acid and 2-nitrophenol) and glutaric- and succinic acid. An usual composition of such a liquor may be: 

25.5 %	adipic acid
25,0 %	nitric acid
6,3 %	impurities.

The rest is water.

The impurities contain a great deal of strong colouring components, the colour of this liquor is between green and black.

The duty of the recovery plant is to produce adipic acid in the required purity out of the very impure reaction liquor.

Because of its use as pre-product for the fiber production the purity requirements for adipic acid are quite high. Normally the following specification must be fulfilled:

adipic acid content min. 99.8 %,
water-content less than 0.1 %,
ash 8 ppm,
iron 0.5 ppm,
colour number max. 1.2 apha-units,
melting point 151.9° C.

Moreover the acid number of the crystals should be as near as possible to the theoretical number. The ester number should be zero. During melting adipic acid should not become dark. So, adipic acid is one of the purest chemicals being produced on a large scale.

Because of its high melting point and because of the sensibility against heat adipic acid preferably will be crystallized out of the reaction liquor.

However, starting with this very impure reaction liquor it is not possible to reach the required product quality by a simple crystallization step.

After separation the crystals produced during single crystallization contain much more impurities and colouring

substances than allowed. These impurities are partly incorporated into the crystal lattice and partly dissolved in the residual moisture.

Only recrystallization, that means redissolving of the so-called crude adipic acid and the subsequent recrystallization leads to the required product quality.

In this scheme there is shown the whole process of the described production line. The reaction liquor from the synthesis is fed into the crude crystallization plant. There it will be divided into the crude adipic crystals and mother liquor. This mother liquor - containing most of the impurities and nitric acid - is recycled into the pre-process. The crystals are fed into the dissolving station where they are dissolved in the recycled heated mother liquor from the pure crystallization. In the subsequent activated charcoal station dye stuff will be eliminated from liquor. The following second crystallization leads to pure adipic acid crystals which are separated from the pure mother liquor. A water-wash in the centrifuge finally guarantees the high product quality. Wash-water and mother liquor flow back to the dissolving station. By purging a certain amount of mother liquor the desired product quality is maintained. By drying the crystals the residual moisture is lowered to figures below 0.1 %.

2.2.2 Crystallization

Of decisive importance for function and economy of the whole preparation process is the choice and the kind of execution of the crystallization process. Incrustation free operation and long continuous operation periods are the required parameters. Due to the rapidly grown theoretical knowledge and practical experience mainly in the last ten years considerable progress in the design

and operation of such crystallization plants could be seen. Older plants were designed for discontinuous operation, so incrustations which were formed during one batch were dissolved by filling the vessel with under-saturated liquor, for the next cycle.

Later on for higher plant capacities and for saving man power it was inevitable to move from discontinuous to continuous operation. Applying the right technical measures to the design and construction of those continuous crystallization plants it is possible to reach incrustation- and trouble-free operation periods of some weeks.

At this place, it should be mentioned that adipic acid is a "pathological" substance with respect to its incrustation tendency.

In the diagram there is shown the solubility of adipic acid in water and nitric acid in different concentrations. In all three cases we see a very strong dependency of the concentration on the liquor temperature. At 20° C there are only a few percent of adipic acid soluble in the solution, whilst at 80° C according to the concentration of nitric acid between 25 % and 40 % of adipic acid can be dissolved.

This is the reason for using a cooling crystallization method in the temperature range between approx. 100 and 20° C. The boiling point elevations of the process liquors lie between 3 and 8° C that means they are relatively low so that we can choose the favourable process of vacuum cooling crystallization. The adiabatic direct cooling of the hot solution without any heat-exchange surfaces on the liquor side is the first important argument for incrustation-free operation.

As we can see from the concentration-temperature diagram the solubility curve has a parabolic characteristic.

This means: adding of hot saturated liquor into cold saturated adipic acid solution will in any case result in a supersaturated mixtures. This is shown in the upper diagram. In comparison to this in the second diagram there is shown a solubility curve with a linear concentration increase versus temperature. Mixing of a hot with a cold saturated liquor in this case results in a saturated solution.

Coming back to adipic acid: The creation of such supersaturations during mixing of hot and cold liquors tends to incrustations in the apparatus. Dependend on the width of the metastable field spontaneous nucleation may arise, also. If it comes to spontaneous nucleation in the crystallizer very fine crystals will be formed. Separation of those crystals is difficult. The residual moisture and the product impurity will increase.

For the solution of this problem it is recommended to use a multi-stage vacuum cooling crystallization. In this diagram it is shown how with increasing number of stages the supersaturation caused by mixing of hot and cold liquor decreases.

In addition to this mixing supersaturation the process supersaturation for the crystallization takes place by vacuum cooling.

Also this supersaturation must be maintained within the metastable region. This is done by liquor circulation in every stage. So the sequence of temperature and concentration points in any stage of such a multistage crystallizer is as follows: initial liquor with a temperature T_0 is fed

into the circulated liquor with a temperature T_E . By this, mixing point T_M which is slightly supersaturated is reached. Coming to the boiling liquid level the superheated liquor mixture is partly evaporated and thus cooled down to temperature T_E . By evaporating and cooling the supersaturation ΔC is reached.

This supersaturation is released by crystallization. The number of stages and the circulation quantity in any stage must be so specified that the resulting supersaturation ΔC is smaller than the metastable region.

Apart from the advantages in the field of crystallization the multistage design is also favourable in respect to energy consumption. As it is shown here by using multistage cooling combined with multistage condensation of the vapours, the cooling water quantity can be remarkably reduced.

To reach the cooling temperature of approx. 20°C that means a vapour temperature of approx. 15°C , vapour compression is necessary for the condensation with cooling water. Also in respect to steam consumption for these vapour compressors multistage operation of the crystallization plant is favourable.

Therefore, some aspects are to be considered:

The required cooling of the liquor - let us say from 80°C in the first stage to 20°C in the last stage determinates the total pressure difference, and according to the selected number of stages the pressure difference between two neighbouring stages.

The product quantity crystallized in any stage should be as consistent as possible. With other words, the supersaturation in all the stages should be equal. Together with the solubility curve this determines the number of stages.

The suspension density should be high enough in each stage to prevent too high rest-supersaturations. 5 % by weight is a realistic minimum figure. On the other hand a suspension density of approx. 25 % by weight should not be exceeded to guarantee a homogeneous suspension flow through the crystallizer.

3. Crystallizer Design

Apart from those process measures for preventing or minimizing incrustations the details construction of such crystallizers has to be done very carefully.

Since a couple of years the horizontal multistage crystallizer is well known. In its simplest form it was mainly used for substances like glauber salt and ferrum sulfat, that means products which are quite easily to crystallize.

This construction consists of a number of MSMPR-vacuum-cooling crystallizers which are arranged in one housing. This results in a compact construction which saves space and money.

In the past it could be shown that this horizontal crystallizer has also advantages for the production of the "pathological" substance adipic acid, if some modifications are introduced.

The liquor transport from one stage to the other takes place by simple overflow of suspension via an overflow-pipe. By this, the level in all stages is kept constant. For simpler cases, the liquor in the crystallizer stages is agitated by so-called air-agitating. In the case of crystallizing adipic acid mechanical circulators must be used in all stages. These stirrers are designed for controlling the supersaturation and for an regular suspension flow in the stages. To minimize crystal attrition relatively big impellers are used with tip speeds of approx. 5 - 6 m/s.

Looking into the crystallizer stages we will find three positions where incrustation takes place. These are the partition wall above the liquor level, the upper part of the overflow pipe and again the partition wall below the liquor level.

During evaporation droplets of liquor are sprayed at the partition wall. Subsequent evaporation at the wall leads to crystallization and to incrustation.

The position of the overflow pipe at the liquor level results in overflowing the highest supersaturated liquor. This tends to incrustations at the edges of this pipe.

Due to the heat flux to the next colder stage another supersaturation will be produced at the partition wall. This is the necessary condition for the growth of a crust.

Such incrustations will be prevented by the following measures.

For the suspension overflow it is important to remove a solution with no or only a small supersaturation. So the position of the overflow-pipe is altered to a very deep point. The simple overflow-pipe is now constructed as an overflow system which is in-

stalled outside the crystallizer. The point of the overflow is vented to the stage from where the liquor comes. By means of a small portion of atmospheric air there is maintained a slight positive pressure difference between the overflow point and the stage. This prevents boiling of the liquor at this point. By the heating jacket around this overflow-pipe cooling of the liquor is prevented.

Insulation of the whole crystallizer reduces the heat flow, that means it prevents cooling of the liquor near the walls. In a safe height above the liquor level small cooling surfaces are installed. At this place a small amount of vapour will be condensed which keeps the side-walls wet. This prevents sticking of droplets or crystals at the wall.

For emergency cases there are nozzles installed inside the crystallizer above the liquid level. From these points the walls can be washed with condensate from time to time if necessary.

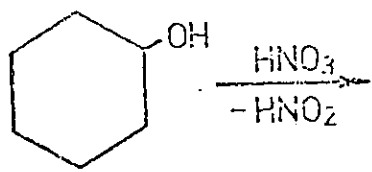
The partition walls between the stages are constructed as double walls. The inter-space is filled with epoxide resins. By this measure the heat flow from one stage to the other is minimized and thus no incrustation takes place at these sidewalls.

4. Operation Results

Here is given a flow-diagram of a built adipic acid crystallization plant including crude and pure crystallization, separation stations, dissolving station, and charcoal towers. 420 t/day of reaction liquor, that means nearly 18 t/h, will be cooled from 90° C to 20° C. Cooling and crystallization takes place in nine stages. During cooling 110 t/day of crude adipic acid crystallize. Vapours of the last four stages are condensed in a two-stage direct condenser. Vapour from the last stage is compressed by means of

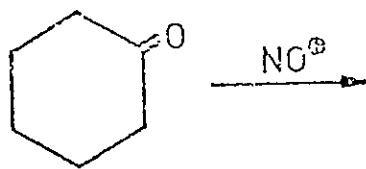
steam jet ejector. The vapours for the first five stages of the crystallizer are condensed in surface condensers to win flush water. The separation of the crude crystals having a mean diameter of 0.4 mm is done by a pusher type centrifuge after pre-concentrating the slurry to a suspension density of approx. 50 % by weight. A part of the filtrate which is pumped back into stage six of the crystallizer to control the suspension density to the desired figure of 22 % in the last stage. The rest of the filtrate and the overflow of the preconcentrator, that means the mother liquor of the crude crystallization - containing most of the impurities - is purged back into the pre-process. The crude adipic acid crystals with a moisture of 4 % are fed into the dissolving station in which also the cold mother liquor from the pure crystallization is pumped. By means of a heat exchanger the mother liquor is re-heated to 90° C. The resulting 40 % adipic acid solution is decolourized in the charcoal station and is now being fed into the pure-acid crystallizer which is identical to this in the crude crystallization.

The produced pure adipic crystals with a mean crystal size of approx. 0.35 mm are pre-concentrated and separated in a pusher type centrifuge equal to the technique described in the crude product.



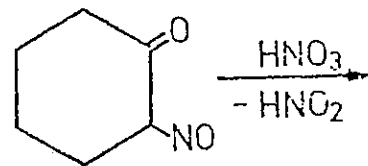
Cyclohexanol

a)

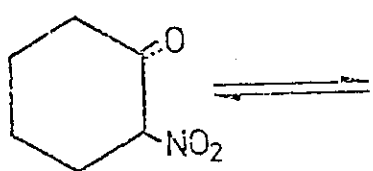


Cyclohexanone

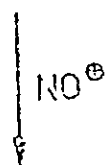
b)



c)

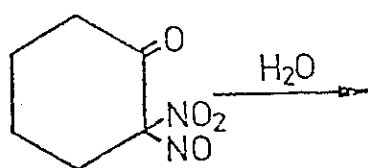


d)

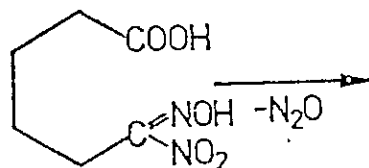


e)

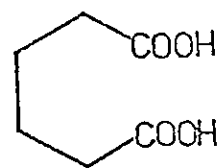
Picric acid,
2-nitro-phenol



f)



g)

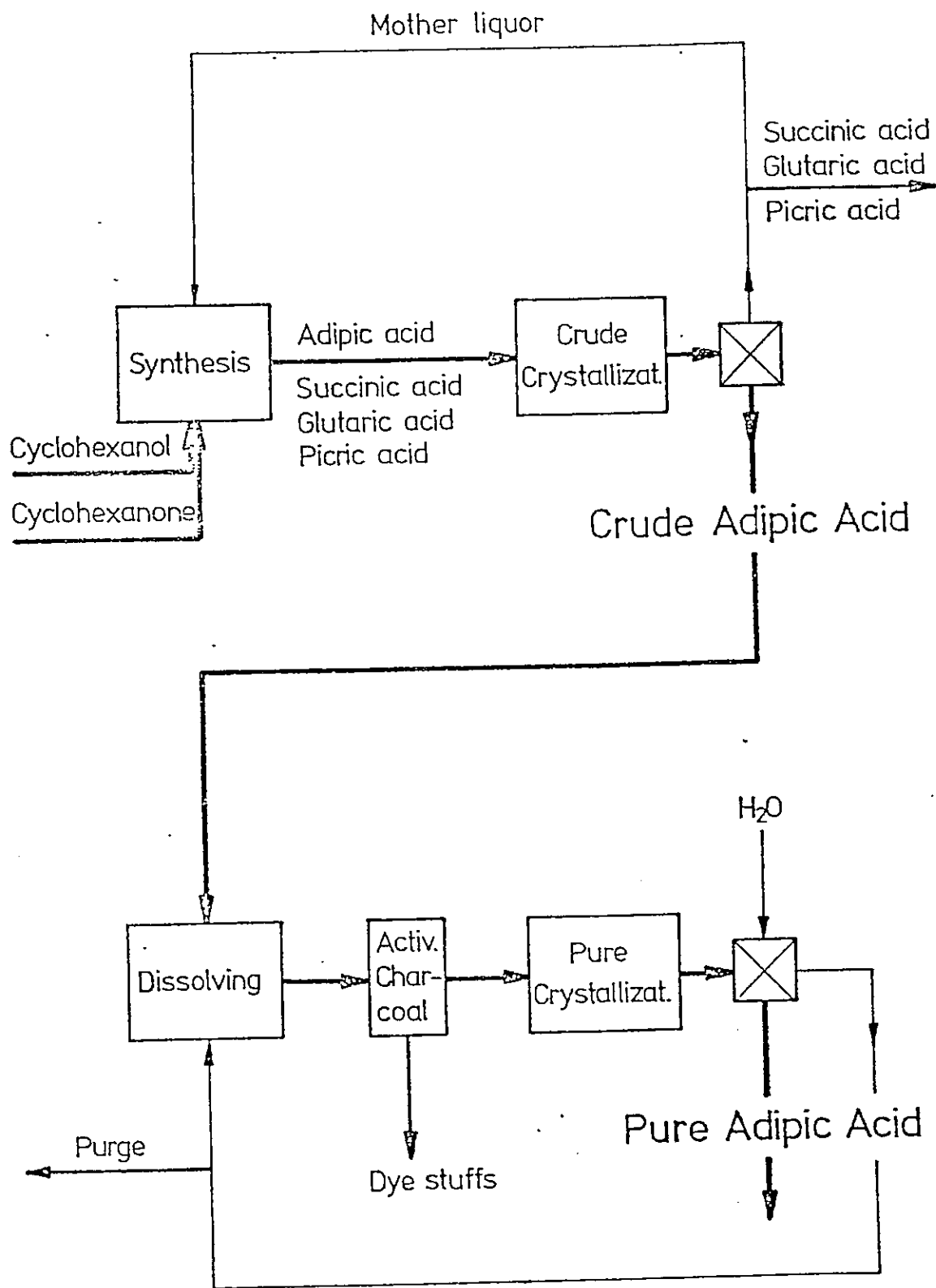


h)

Adipic acid

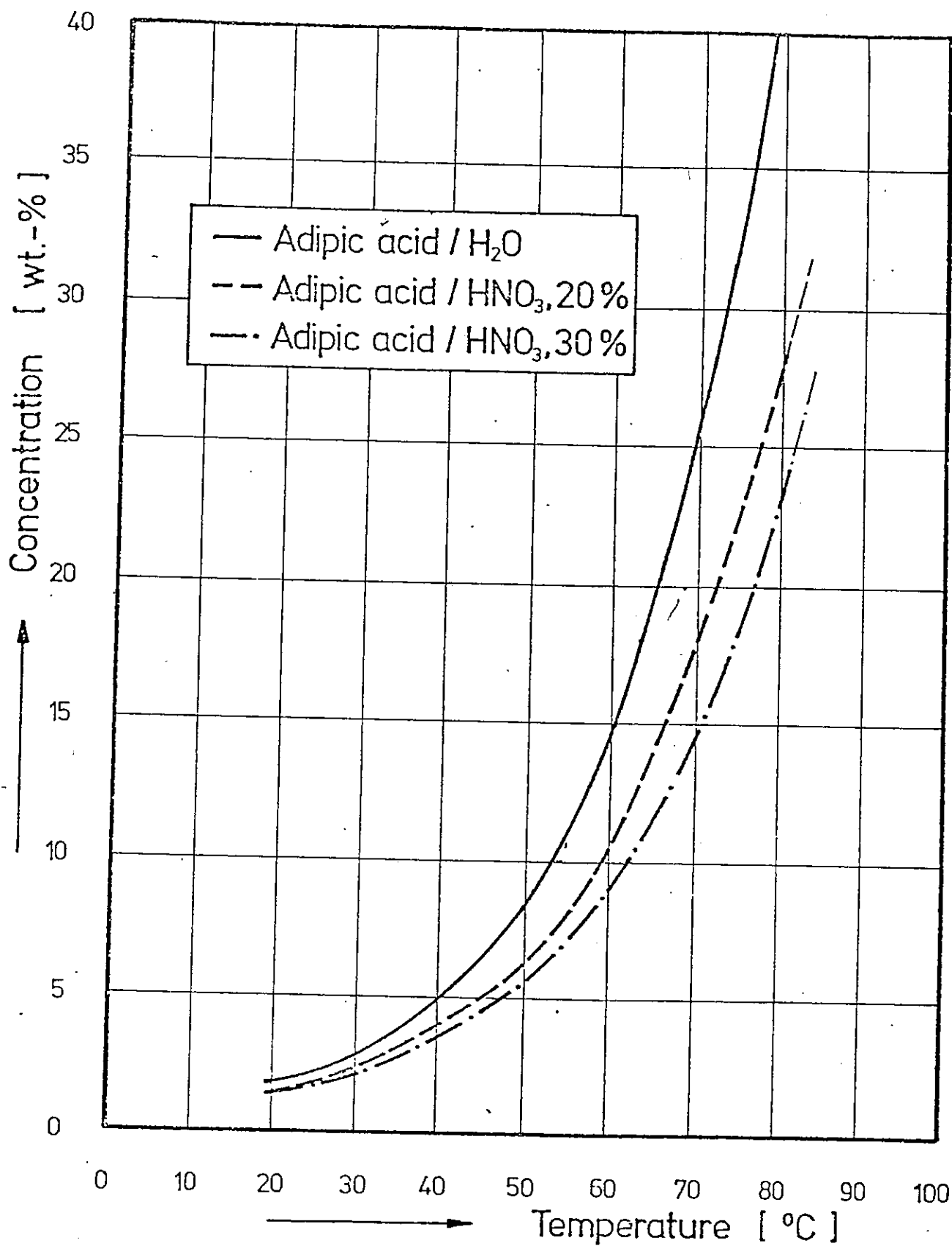
Synthesis of Adipic Acid

Fig. 1



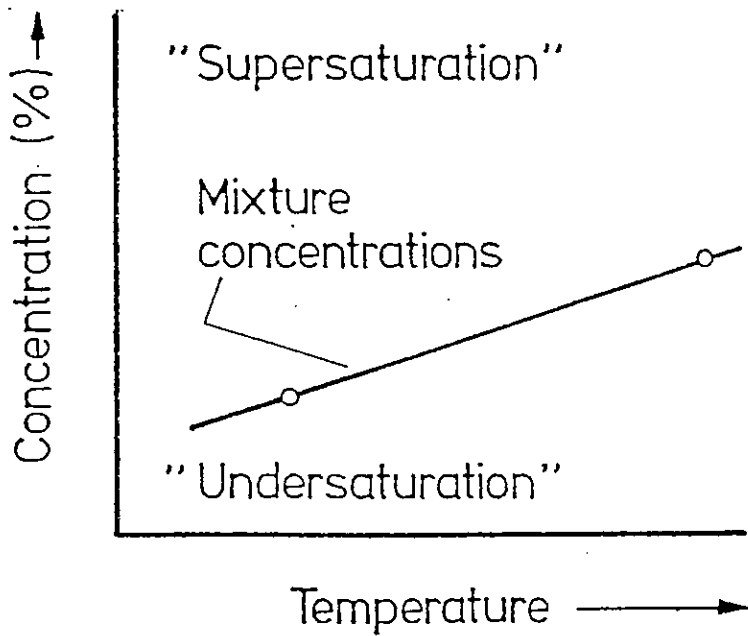
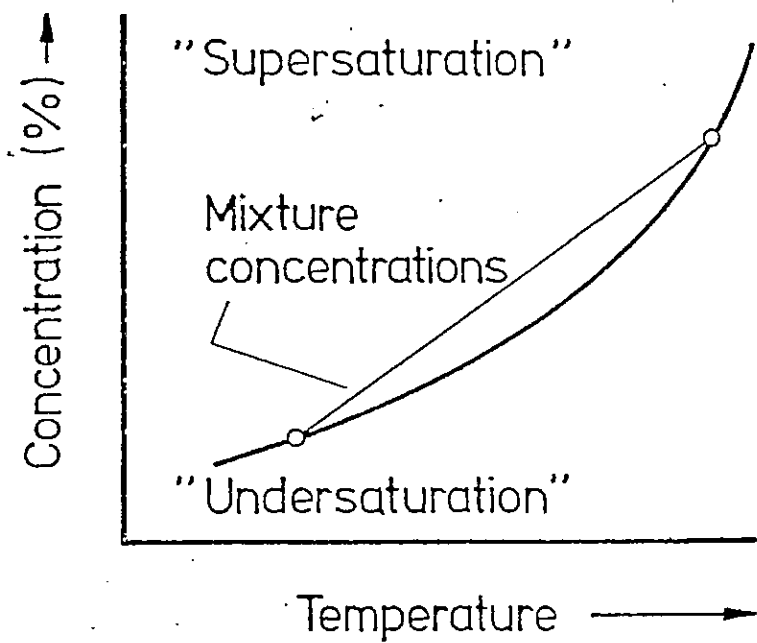
Preparation of Adipic Acid

Fig. 2



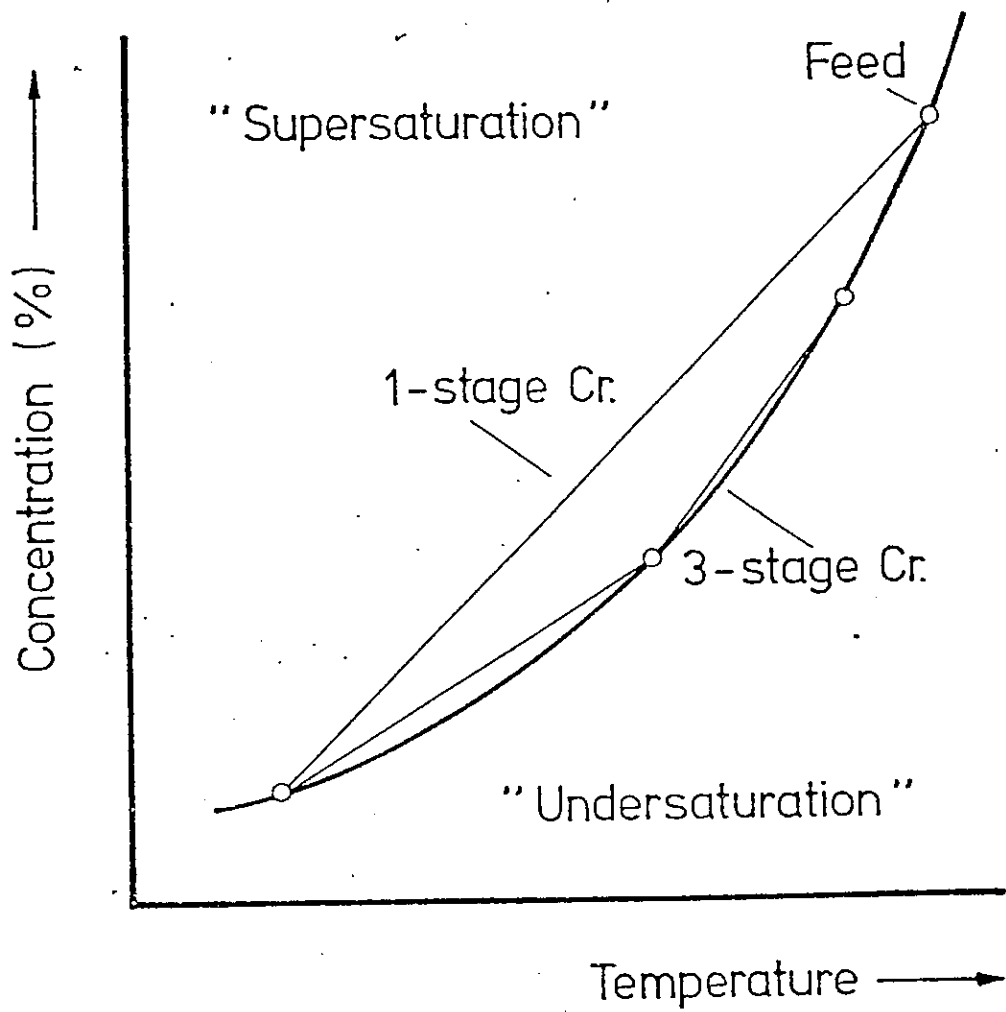
Solubilities of Adipic Acid

Fig. 3



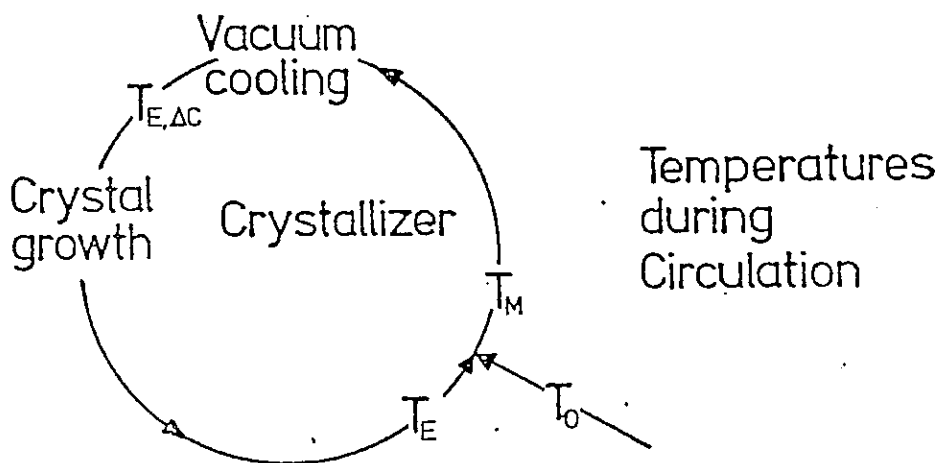
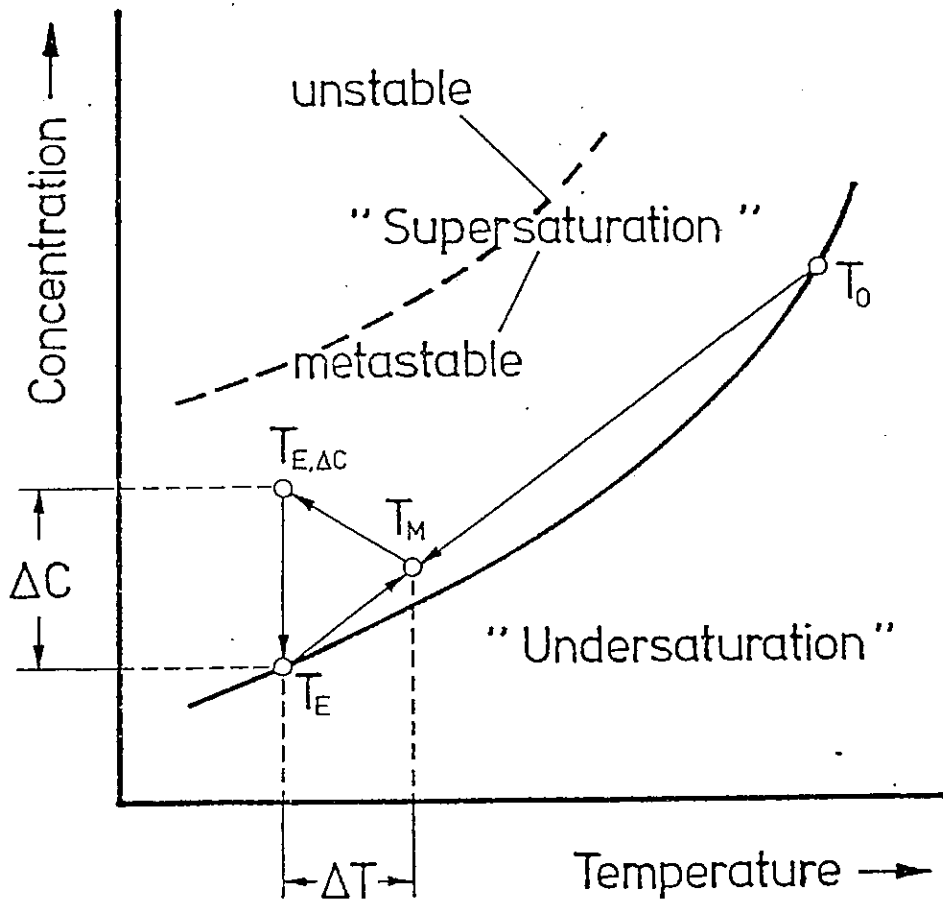
Supersaturation of Mixtures
only at Nonlinear Solubility

Fig. 4



Supersaturation of Mixtures
as f (Number of Stages)

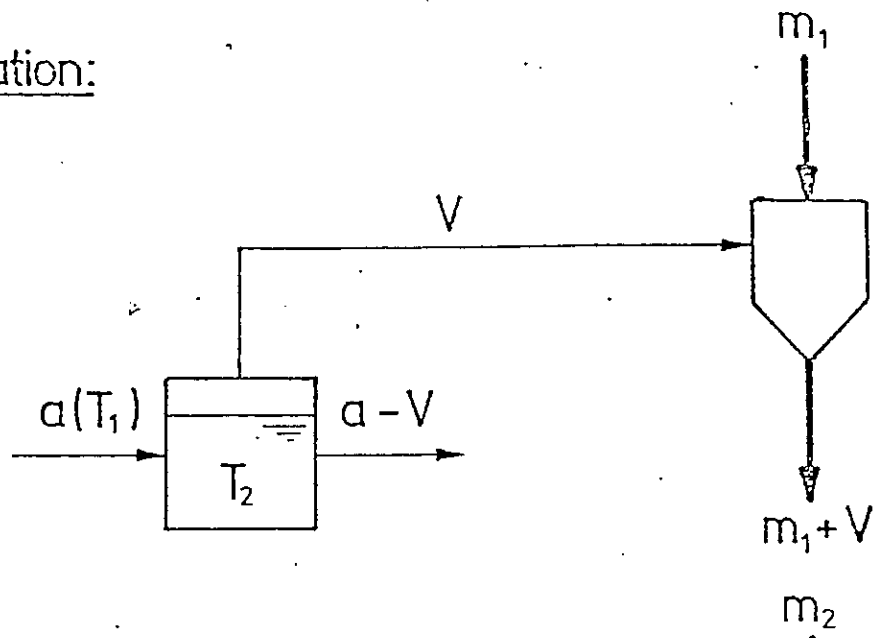
Fig. 5



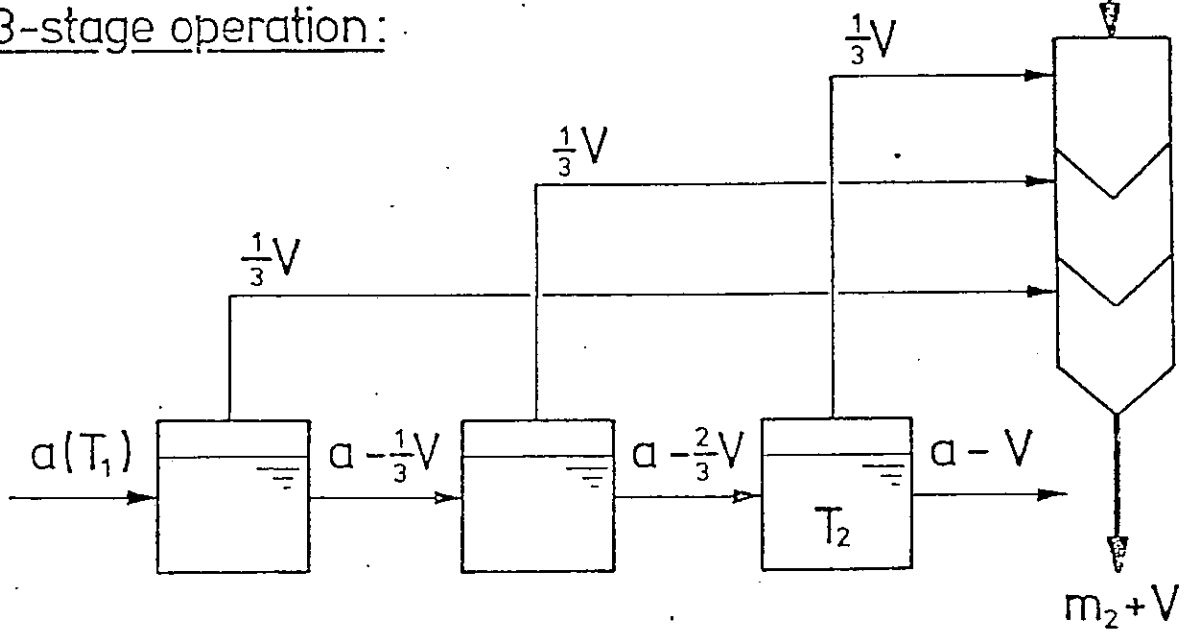
Control of Supersaturation

Fig. 6

1-stage operation:



3-stage operation:

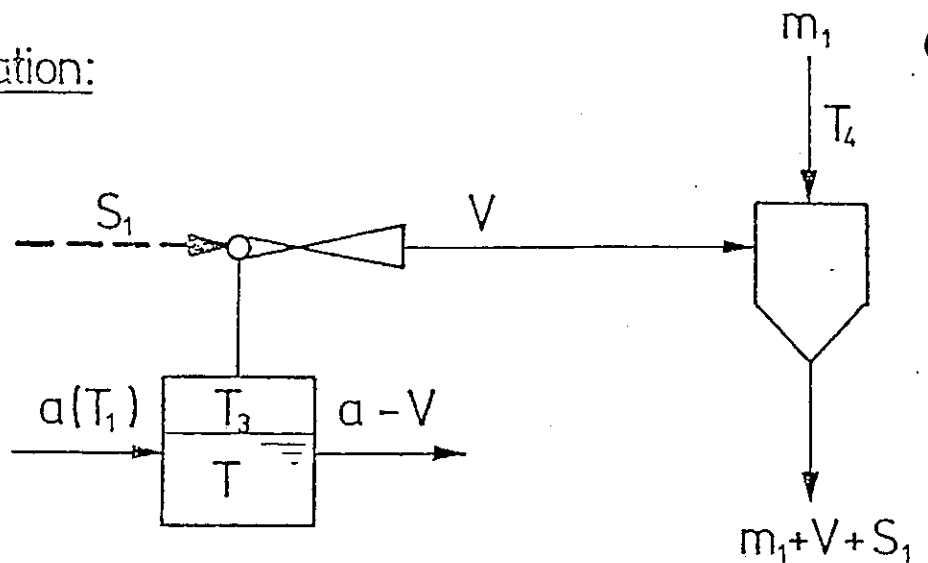


Result: $m_1 > m_2$

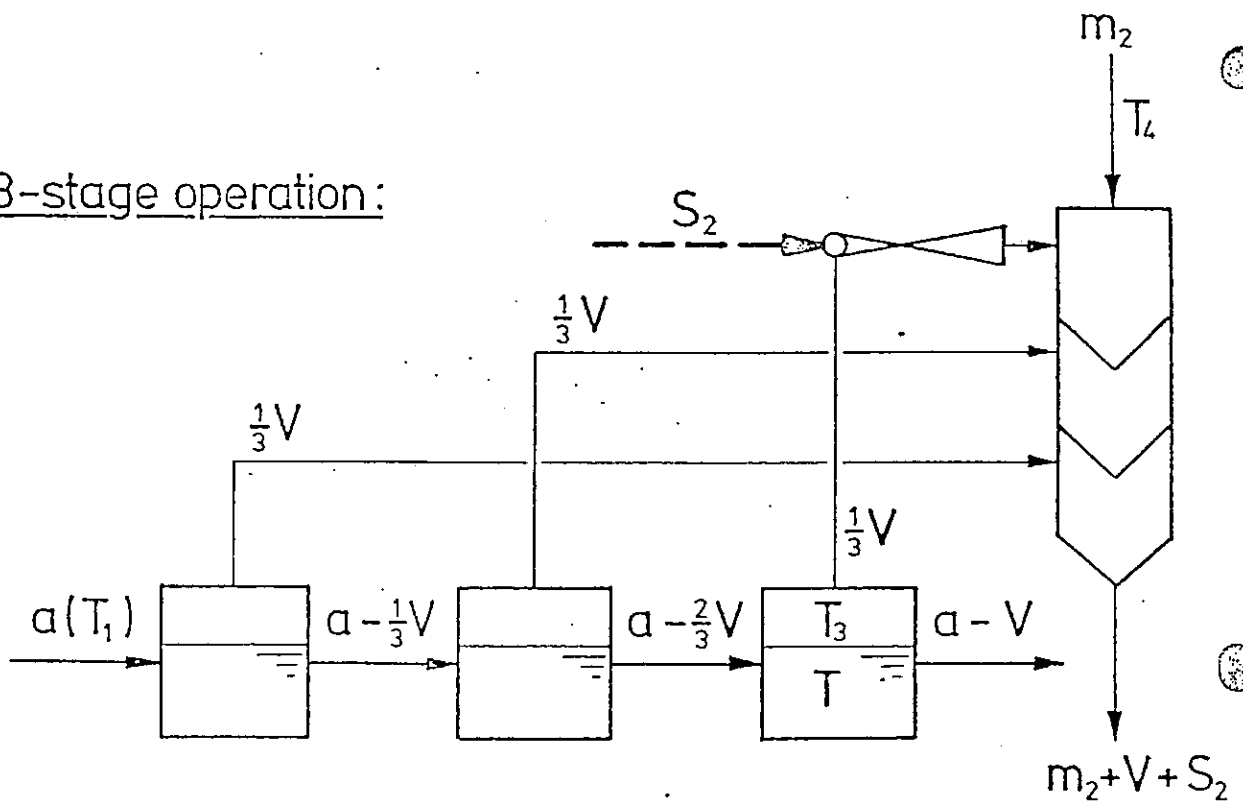
Cooling Water as
f (Number of Stages)

Fig. 7

1-stage operation:



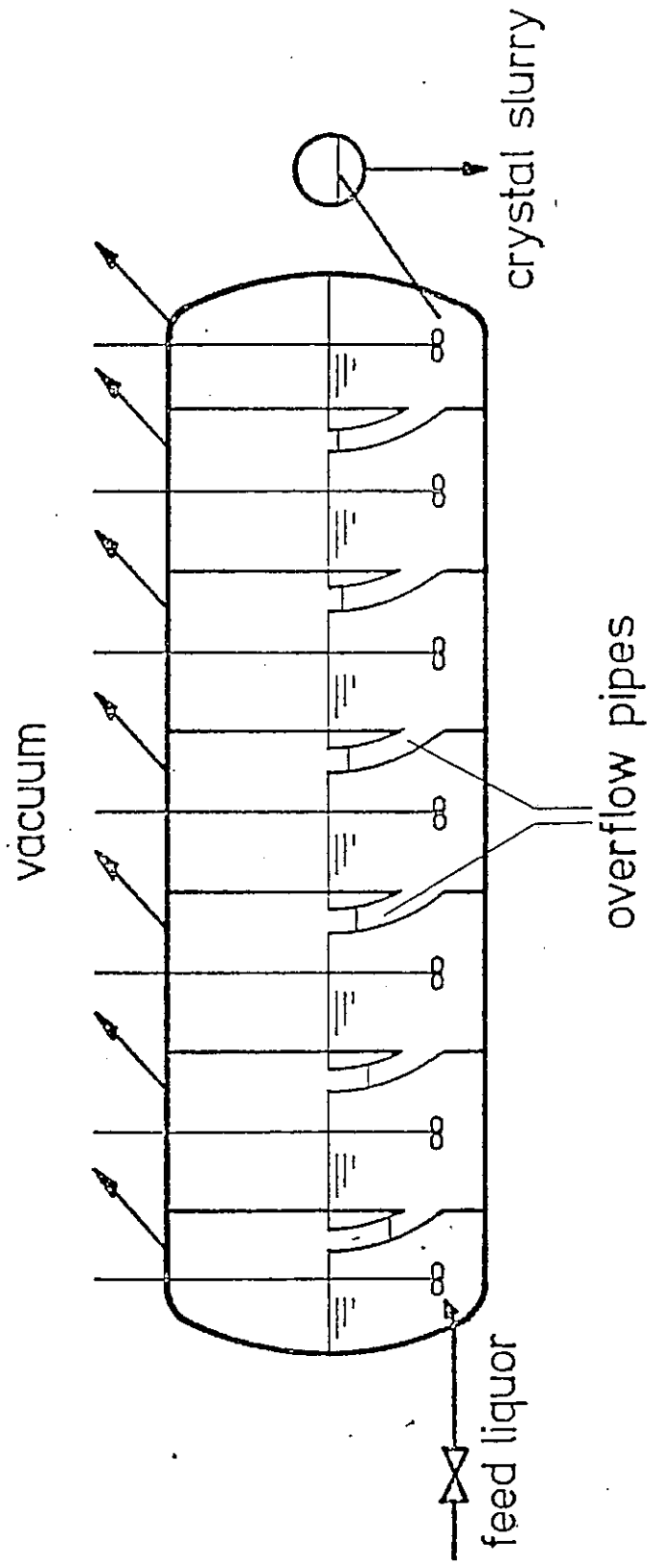
3-stage operation:



Result: $S_1 > S_2, (T_3 < T_4)$

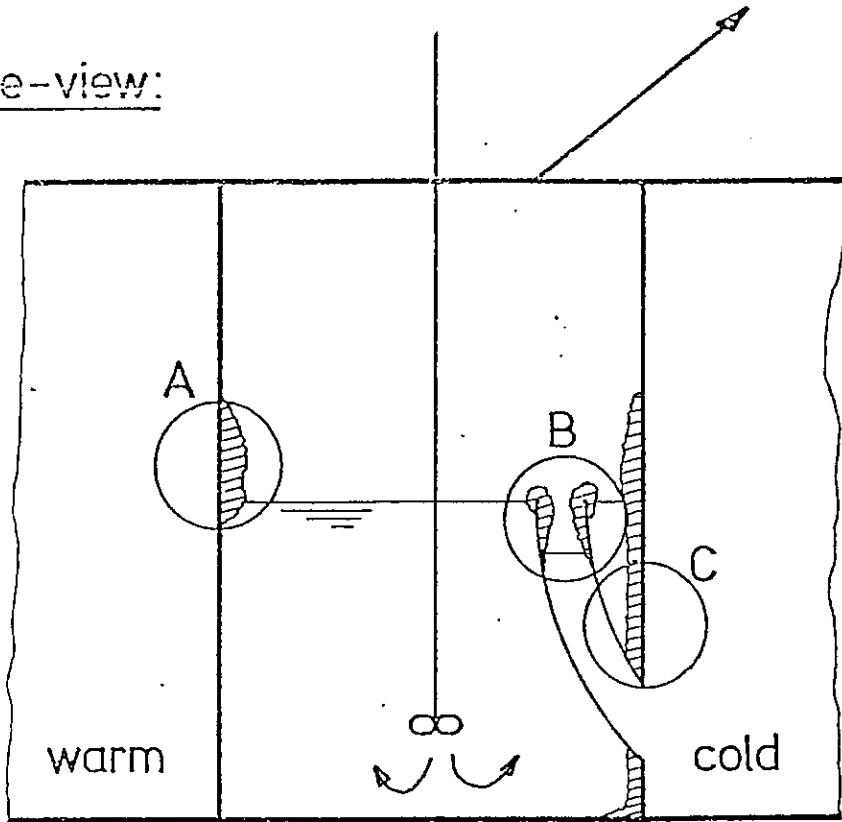
Steam Consumption as
f (Number of Stages)

Fig. 8

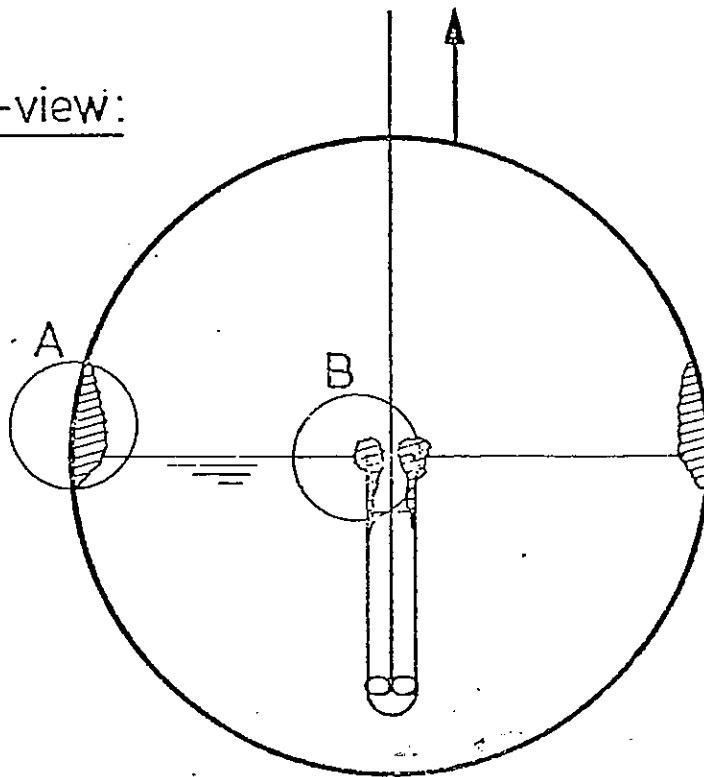


Horizontally Arranged Vacuum Crystallizer, Conventional

side-view:

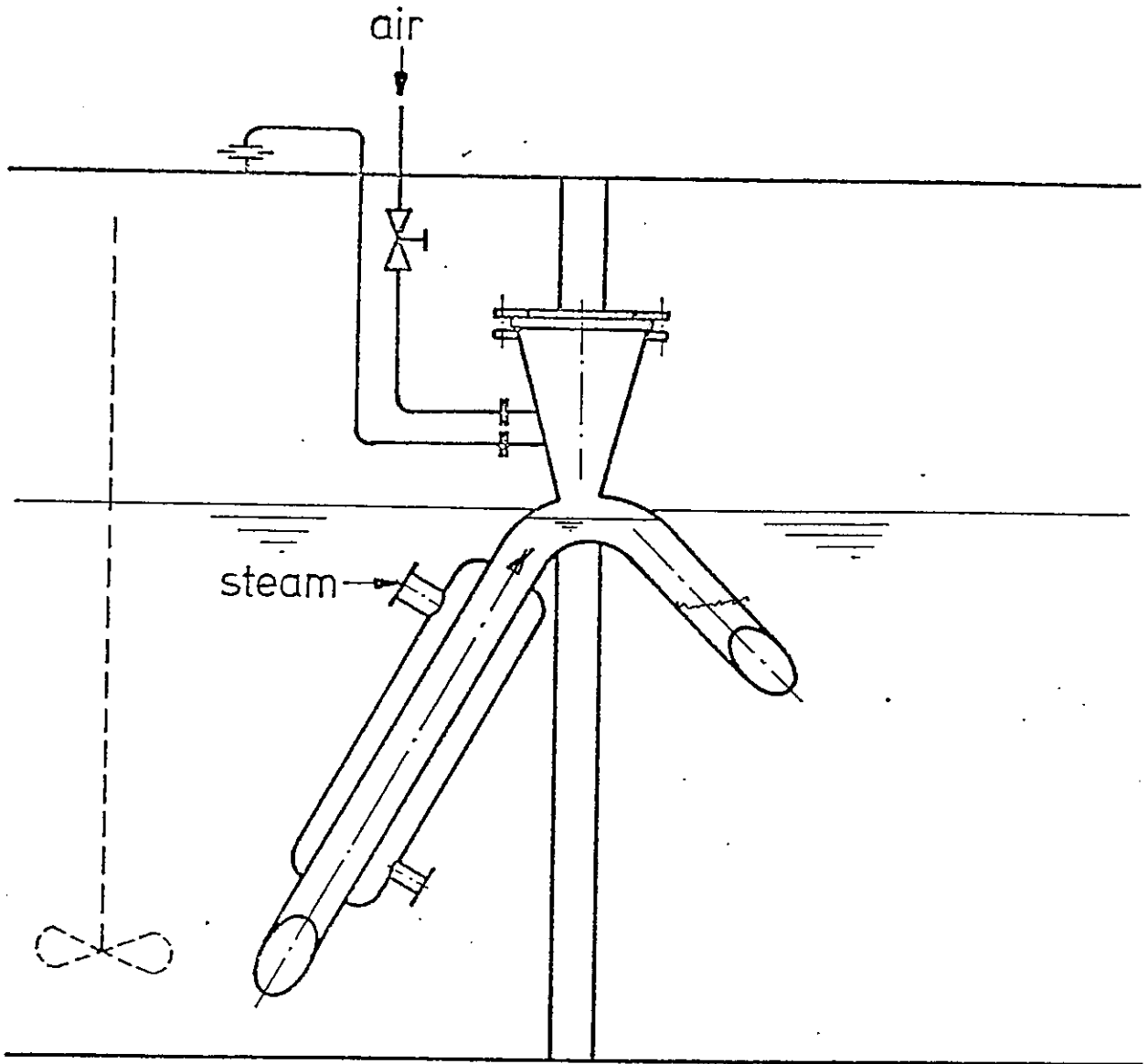


front-view:



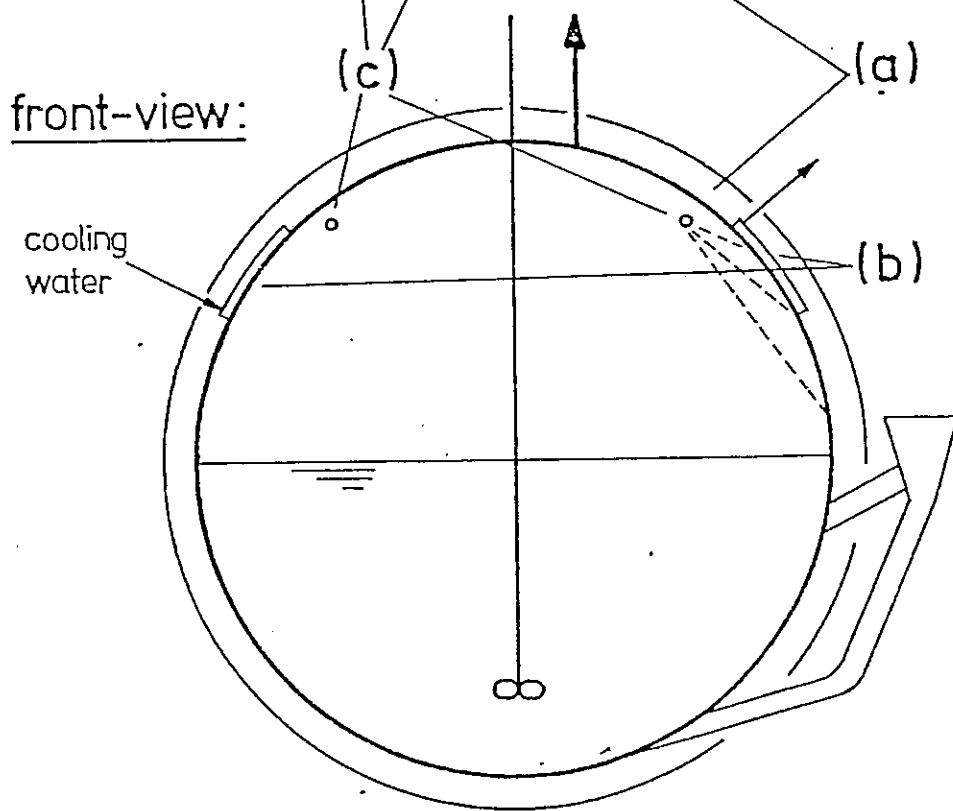
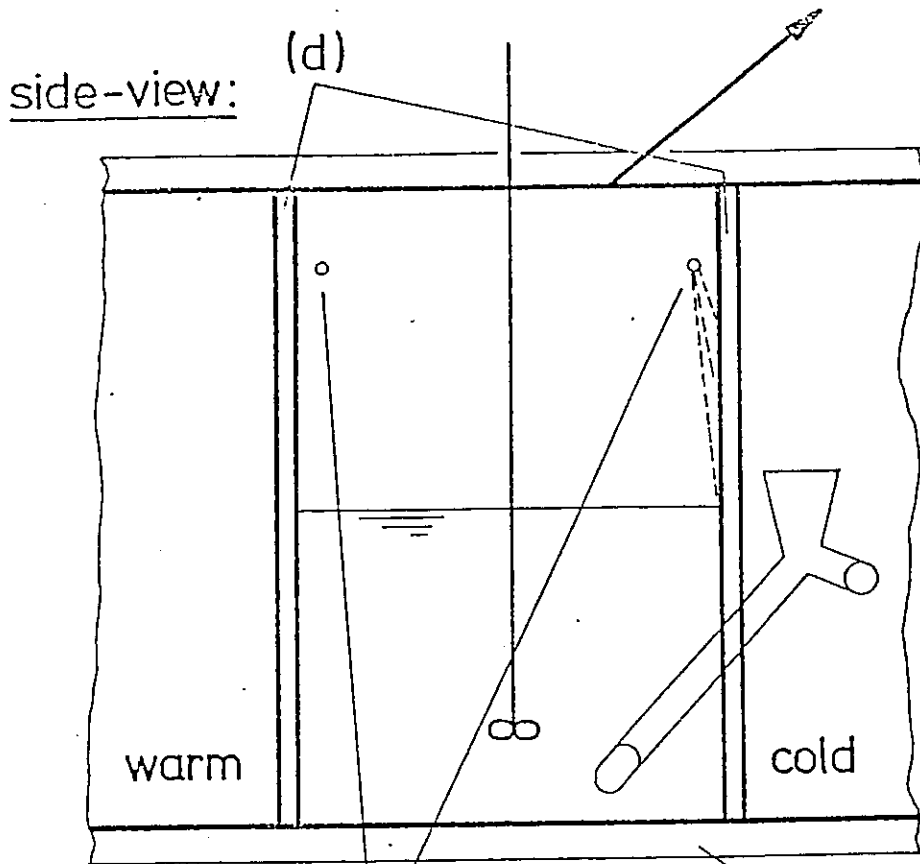
Most Probable Positions of
Incrustations

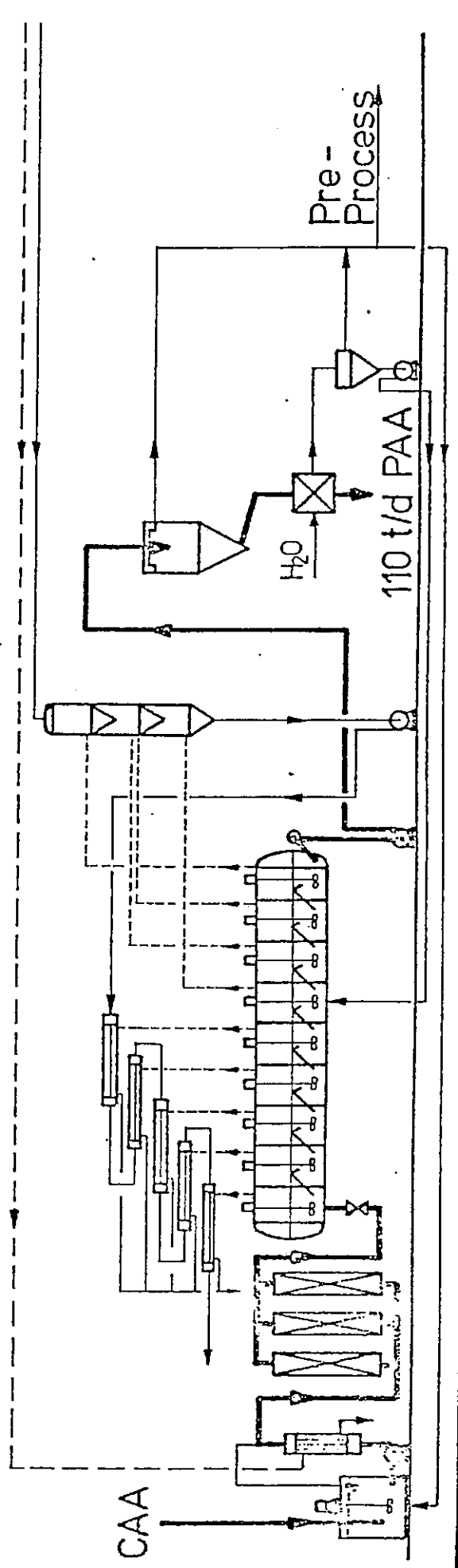
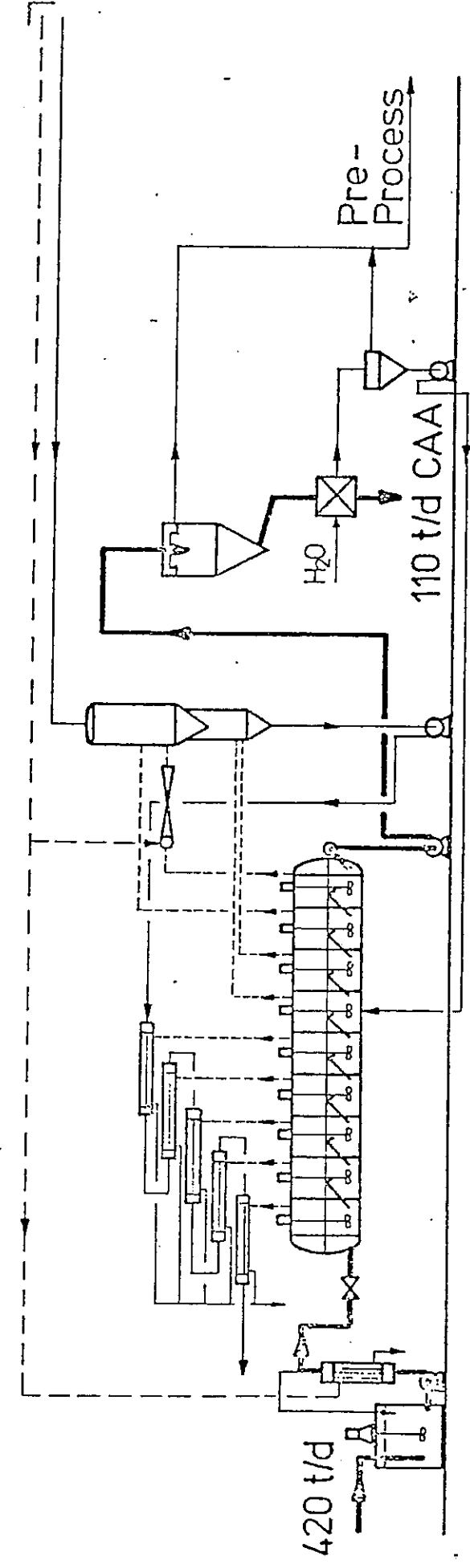
Fig.10



SMD Overflow Pipe

Fig.: 11





Flow Diagram
Adipic Acid

Fig. 13