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Trends of Industrial Crystallization - Processes

W. Wöhlk, G. Hofmann

MESSO-CHEMIETECHNIK GmbH, Duisburg, Germany

1 Introduction

The use of crystallization is nearly as old as mankind itself. In spite of this, industrial crystallization still is a young technology. Although industrial-scale crystallization plants were built already hundred years ago, tailor-made crystallization became possible only with establishing of the theoretical backgrounds. These have been worked out during the last thirty years, leading to the fact, that crystallization still is a field with above average development resources.

This, going in parallel with increasing demands for process and product qualities by reasons like environmental care, energy savings or product properties, is a remarkable driving force for setting new applications of crystallization in processes today. These modern processes, with the use of advanced crystallization technology, of course must also meet the virtues in plant engineering, like:

- reliable integration of all unit operations forming the crystallization plant
- safe and easy to operate and to maintain
- easy to control also in partial load situations
- highest availability together with minimized equipment price and operation costs.

Two developments of the last years being typical for the todays' requirements for special problems solutions in the field of crystallization are described below.

2 Crystallization of Caffeine

This example demonstrates, how by knowing the capabilities and limitations of the unit operation crystallization and tailor-made assembling of different unit operations an unique crystallization process can be formed to meet the target.

The conventional technology for decaffeining coffee is the extraction with solvents. Still today it is common practice to use chlorinated hydrocarbons as solvents, which are known to be the most dangerous ozone-layer killers. Meantime, however, an alternative process is already on the way to displace the common technology. It is based on the use of supercritical carbon dioxide as solvent for extraction /1/. CO₂ is harmless with regard to the environment and of course the product remains completely free of solvent. Furthermore, the extraction with carbon dioxide is extremely selective. No undesired substance is extracted from the green coffee-beans, which after roasting contributes to the typical taste and flavor of coffee. Coffees with and without caffeine accordingly differ from each other only by their pharmaceutical effects.

For decaffeining of coffee using that new technology, the pre-steeped green-beans are treated with carbon dioxide under a pressure of 160 to 220 bar at temperatures between 70 to 90 °C. The caffeine diffuses from the beans into the supercritical carbon dioxide, which in the next step is transported into a washing column, where the caffeine is extracted into water. Whereas the regenerated carbon dioxide is recycled, the caffeine-containing wash water has to be replaced by fresh water. This requires a quite high consumption of fresh water (3 to 5 kg/h per kg green coffee), the caffeine concentration in the used wash water is maintained at the low level of 1.4 to 10 g/l /1/.

The fresh water must be prepared before use to keep product quality, and the caffeine containing used water needs treatment before discharging. Both leading to operation costs, which cannot be neglected. A solution for this is given by a process idea (see Fig. 1) which allows to recover the water, and at the same time isolates the valuable natural caffeine.

The process as a whole is feasible only, if the caffeine is produced in an appropriate quality for the use in pharmaceuticals. Consequently recovery of caffeine becomes to a key unit operation for the decaffeining using CO₂.

The process requirements are given by the used water composition and the specification for pharmaceutical caffeine (Fig. 2). On the very first view it appears clear the process has to consist of a water recovery and a crystallization step, at least.

For the development of this process a first evaporation and subsequently crystallization trials were carried-out in bench-scale. Without any problems evaporation proved to be suitable to recover a condensate of the desired water quality.

However, meeting the product specification during crystallization, it was more complicate. Caffeine is known to crystallize in two modifications, the anhydrite and a monohydrate. The transient point is somewhere between 70 and 50 °C. Crystals were reported to be extremely long, matted together and hairlike needles /2/. Our first products however, showed compact particles, rod-shaped and sometimes also like potatoes with a brownish colour (Fig. 3). Even with recrystallization it was not possible to produce the desired product quality.

Some decomposition of caffeine was recognized to be responsible for this behaviour, which was nearly independent on temperature. As reason, oxidation by air oxygen was isolated, immediately forming dark brown liquors when air was re-contacting solutions after vacuum evaporation. Literature reports hydrolytic decomposition to caffeidine dicarbonic acid and caffeidine in alkaline solutions /3/, whereas caffeine is said to be remarkably stable in neutral or acid solutions.

Evaporation trials with acidified solutions already brought a strong improvement. Decomposition by oxidation was depressed, and after treatment with activated carbon a caffeine of pharmaceutical quality was produced. The crystal shape this time was that known from literature, i.e. very long, hairy needles, especially, when crystallization was done in unstirred solution by cooling over night, pointing out the impurity to be a strong habit modifier.

The treatment with activated carbon is one of the known alternatives to recover the caffeine from the extraction effluents /1/, because activated carbon adsorbes caffeine very strongly. As the production capacity for caffeine is always in the range of kilograms only, even for big decaffeining units, a treatment with activated carbon takes strong influence to the process yield. As adsorption is a function of concentration the losses via activated carbon treatment are dependent from its location in the process. With regards to the best purification effect the treatment is best located in front of crystallization; with regard to losses the best location would be in the weak solution before evaporation.

After all the position of the activated carbon station in front of the evaporation was found to be best.

Consequently, the resulting process is assembled by the process steps (Fig. 4):

1. Treatment with activated carbon
2. Filtration
3. Evaporation with minimized retention time
4. Crystallization with mother liquor recycling to 1.

A possible design of the plant is presented in (Fig. 5). The caffeine-containing wash water entering the plant, at first is slightly expanded, allowing the carbon dioxide leaving with the vapours. Activated carbon powder is added to the solution after pH-adjustment. After adsorption the suspension is separated, the sludge wasted and the purified liquor given to evaporation. This example shows a concept consisting of falling-film evaporators with mechanical vapour re-compression and solution preheating against the vapour condensate. The density-controlled concentrate then is given to the crystallization unit. Retention time in the evaporation must be kept low to minimize product decomposition.

The solubility of caffeine in water is moderate with a certain temperature dependence (Fig. 6). Regarding the low solubility and the temperature sensitiveness the cooling principle recommends itself as crystallization process. The always very small production capacities in the range of some kilograms per hour make it advisable to choose surface cooling crystallization, either in continuous or discontinuous operation. Because of the very high demands for product quality and the continuously operated adjoining process parts there are advantages for continuous operation even in this case of the very low production capacities.

The cooling has to be carried out at a low temperature to minimize product losses with the purge. This purge controls the impurity level. The task for crystallization is more or less reduced to solidification and good separability of the formed crystals as the solution is already purified by the process steps before crystallization. Thus, also the crystallizer is reduced down to its essentials. It is characterized by a ring pipe, in which heat exchanger, retention time vessel and circulation pump are connected in series. No special regard is taken to minimize either crystal attrition nor secondary nucleation, because the hairlike-shaped, tiny crystals are broken down anyway and afterwards also the crystallized monohydrate loses its shape during the required calcination. (A similar design, but with a special attrition-reduced circulation pump is shown in Fig. 16). Instead of this, special equipment was assembled for sufficient separation, drying and calcining.

For the production of caffeine crystallization is the right and only process choice. In addition to the crystallization step, however, some other operations must be introduced to meet the required product specification in the crystallizer. The development of such a process requires at first the knowledge of the crystallization to judge their possibilities.

A first plant for a capacity of 10 t/h water evaporation was realized in 1991. The quality of the caffeine produced has fulfilled the market demands already from the very beginning.

3 Melt Crystallization In Solution Crystallizers

The market for organics notes increasing need for pure and ultrapure substances since years. This situation has forced a steady development of all material separation processes and melt crystallization has been drawn into more attention as alternative to rectification, extraction or solvent crystallization. Research and development in this field have been accelerated and large-scale applications are already common practice in some places.

Melt crystallization is especially used, when distillation fails due to special physical properties of substances or phase systems. That is the fact for substances with directly neighbored boiling points, for azeotropic systems and for the purification of temperature-sensitive products. Also advantages on the energy side are standing for melt crystallization, because heats of crystallization are smaller than heats of evaporation. Besides this, crystallization is executed at lower temperature levels.

All these considerations and activities are based on the view of melt crystallization to be a completely separate unit operation beside the crystallization by the use of solvents with some exceptions all crystallization jobs in organic chemistry used to be solved by the so-called melt crystallizers, all in inorganic chemistry by solvent crystallizers. Even for the design of melt crystallizers there has been no loan from solvent crystallizers. This nearly complete independence stands in a surprising contrast regarding relations. In fact, transitions are smooth.

The common definition of melt crystallization might have supported this separation from solvent crystallization. That is: "Melt crystallization is the concentration resp. isolation of substances by use of the phase transition melt/crystal without the use of solvent(s)". In fact, also melts can be defined as solutions of the molten resp. participated components.

A good example for the overlappings between melt and solvent crystallization is given by the phase system bisphenol A - phenol, a mixture which is produced as an intermediate in the synthesis of bisphenol A. In (Fig. 7) this system is represented as the commonly known melt diagram. It can be defined as a peritectical system, in which three pure crystalline solids, namely bisphenol A, phenol and a crystalline adduct of one molecule bisphenol A with one molecule phenol do exist. Mixed crystals, resp. solid solutions, are not formed. From those phase systems the pure substance can be isolated in only one theoretical stage, no "fractional crystallization" is necessary.

The same phase system can be shown as a solubility diagram in (Fig. 8). In this figure the bisphenol A is defined as the dissolved component. Beside the eutectical point this system has a second invariant point (B), in which the two solids bisphenol A and the phenoladduct coexist. Along the saturation curve A to B the pure adduct (a solvate of bisphenol with phenol in the ratio 1:1, like the monohydrate in hydrous solutions) is formed and above B the pure bisphenol A. From the slope of this saturation curve it easily can be taken - regarding the strong temperature dependence - that in principle both solids can be isolated by using the single cooling crystallization from solutions. Per definition, the second component phenol is simply be seen as a solvent.

Comparison of the techniques

Melt crystallization

Meantime, several processes are established. They can be characterized as follows:

- i) Processes with melt crystallization on cooled surfaces, forming crystal layers (freezing). These are operated batchwise or semi-continuous, also in large-scale units.
- ii) Processes with melt crystallization, forming crystal suspensions. These are most operated continuously.

In the processes under i) the residual melt is separated only by natural gravity, i.e. by draining or trickling off. A technical design is the so-called falling-film-crystallizer /4/ in (Fig. 9). Due to the high amounts of residual melt on and in the crystal layers the effect of purification per batch is small. Meeting the desired purity therefore requires several recrystallizations. Crystals and mother liquor are guided counter-currently, and that's why this process can be used for fractional crystallization, allowing the splitting of solid solutions.

Due to the discontinuous operation and the repeated recrystallization the specific crystallization performances are comparably low (5 - 10 t/m³ a). Typical space - time - yields are some 10 to 70 kg/m³ h /5/.

Among the suspension processes in melt crystallization are known stirred vessels with cooling jackets or internal heat exchangers /6/ (Fig. 10). Also these designs have only relatively small specific production capacities, because cooling surfaces are limited and incrustation occurs frequently or even is essential for the function.

A more known design following this principle of suspension crystallization is the Brodie-purifier /7/ (Fig. 11), in which a counter-current flow of residual melt and crystals is aimed for. According to this counter-current flow this type in principal allows fractional crystallization, i.e. splitting of solid solutions. Due to serious problems with the fluidynamics of melts and solids, which very often do not differ sufficiently in specific density, the operation of this crystallizer, some special cases excluded, is difficult to keep under control.

Solution crystallization

As a rule, solution crystallization is operated continuously, with an exception for small production capacities. The crystallizers are fully developed and optimized for the production of good separable crystals long ago /8/. In opposite to melt crystallization the CSD's of the products are of special interest. Therefore, special growth-type crystallizers were developed. In these types (DTB- and Oslo-) some special devices support the production of coarser crystals, providing especially the attrition minimized handling of the crystal suspension.

Fig. 12 shows the three basic types of industrial solution crystallizers. From these, all known types of solution crystallizers can be derived. In all these types supersaturation is controlled by a directed circulation, which is done by marine impeller pumps, either in elbow or draft-tube position /8/.

Supersaturations are kept small by high circulation rates, allowing the control of particle formation and crystal growth. Moreover, this offers excellent conditions for heat exchange, e.g. for the use of tube-bundle heat exchangers, causing good heat transfers and permits incrustation-free operation, due to the turbulent flow patterns. The heat exchanger can be taken for heating and for cooling as well, i.e. the types can be used for evaporative crystallization as well as for cooling crystallization.

Applicabilities for Solution Crystallizers in Melt Crystallization

Also for melt crystallization the use of surface-cooling crystallization is common practice. Therefore, it nearly suggests itself to use the surface-cooled solution crystallizers also for melt crystallization, for the most part leading to remarkable advantages in specific crystallizer performance, space-time-yield and energy consumption.

These types are best suitable for single crystallization. Fractional crystallization is theoretically possible by counter-current connection of several stages or by batchwise operation with storage technique, but not practised usually.

Consequently, for the use of solution crystallizers in melt crystallization there are the following pre-conditions:

- due to the typical large circulation rates only phase systems with lower viscosities (below 100 mPa s) can be handled,
- the substance to be crystallized must not form solid solutions.

It is hardly to estimate, which percentage of phase systems in question do meet the first condition, because temperature offers one additional degree of freedom. However, the number should be rather high.

For the second pre-condition there are some indications in literature. Rittner and Steiner /4/ report a majority for eutectic systems. Matsuoka and Fukushima /9/ used the International Critical Tables /10/ as reference and found 80% of the phase systems with two components to be eutectic systems (Fig.13).

This stands for the fact, that a big majority of separation problems in organic chemistry could be solved by using the principle of single crystallization. Even the circumstance that some of the minor concentrated but nevertheless important impurities may cause transformation into systems with limited miscibility (as it is the case in the presence of some thio-compounds) cannot really change this statement. In those cases the single crystallization has to be understood as a pre-purification method.

Actually, these statements are supported by numerous not fractional crystallization processes, which have been in use in organic chemistry since decades. Substances, produced that way, are: caprolactam, naphthalene, p-chloronitrobenzene, p-xylene, p-dichlorobenzene, p-cresol and bisphenol A. These are crystallized without any solvent, but with the techniques of solvent crystallization. Most of the crystallizers are self-made constructions. Also for revamping of these processes the solution crystallizer therefore can be a recommended alternative.

Using the example of bisphenol A - crystallization the possible advantages of melt crystallization in a typical solution crystallizer are described below.

4 Crystallization of bisphenol A - phenoladduct

In the presence of acid catalysators bisphenol A can be synthesized by condensation of phenol with acetone [11,12]. The condensation is carried out in excess of phenol in presence of strong acid or strong acid cation-exchanger material and accelerators, sometimes. The result is a crude product, which beside bisphenol A contains not reacted phenol and acetone, catalyst, the accelerator and some undesired co-products, like the codimeres, condensation products like trisphenol or still higher condensed products in form of tarry and high-boiling substances.

For the isolation of the pure bisphenol A most of the manufacturers today are practising the crystallization of the phenoladduct instead of fractional distillation (Fig. 14). At first, the condense water and the excessive acetone is taken off by distillation from the synthesis liquor before crystallization. Acetone is recycled into the reaction and the resulting melt is fed to crystallization. Temperature is between 70 to 80 °C, crystallization is carried out at temperatures slightly above 40 °C (compare Fig. 15). A suspension of bisphenol A - phenoladduct crystals is formed. The mechanical separation properties of this suspension and the purification effect by crystallization as well as the incrustation-free operation cycles are guidelines for the economy figures of this process.

For further treatment the mechanically separated phenoladduct is molten and the phenol distilled. The resulting and already quite pure melt of bisphenol A is further rectified and finally solidified. The quality of the mechanical separation process is given by the CSD achieved and the habit of the crystals produced. For that reason the crystallizer design has to be adapted to the special requirements of those organics.

The crystal habit cannot be influenced easily. A tailor-made for the crystal habit, e.g. a pointed addition or removal of impurities - if admissible at all - so far is not possible still today. In this case of bisphenol A, the crystals are very weak and bundles of very tiny needles. Therefore special care has to be taken to minimize crystal attrition and breakage.

With regard to the kinetics of crystallization, the crystal size distribution and the mean crystal size are the consequence of balancing the influences of crystal retention time, resp. suspension density and mechanical stress in crystallizer design /8/. The more the crystals are stressed mechanically, the more the attrition rate takes influence to the effective crystal growth rate. Mechanical stresses may lead to the fact, that crystal size becomes independent from retention time or even decreases with retention time /13/. Even more this is valid for needle-like crystals. Therefore, crystallization of organic products needs a special preserved handling of crystals and crystal suspensions.

The withdrawal of suspension from the crystallizer for example, therefore should be free-falling without using pumps. For the internal circulations the marine impeller pumps of the growth-type crystallizers are acceptable. These pumps are special developments with slow rotating impellers of exceptionally large diameters. Beside this, the efforts in minimizing attrition are supported by the very low density differences between solids and liquids in many organic systems - what is fact especially for the bisphenol A - system. These small density differences are the reason for narrow demixing behaviour of suspensions in crystals and liquors, leading to the fact, that the impacts between crystals and impeller - usually the main source of attrition and nucleation - are remarkably reduced in strength.

For a comparable problem in the field of solvent crystallization already some years ago a special crystallizer modification was developed /14/. This type was adapted for the crystallization of the phenoladduct by replacing the circulation pump with a special attrition-minimized impeller pump, as discussed above (Fig. 16).

The design of this crystallizer is a reduction to the essentials. The typical directed circulation is dominating the design, here a ring construction formed by the circulation line. The circulation pump is set on top as elbow-pump. This position was chosen, to reduce the risk of phenol leakage. A further contribution to process safety is given by the fact, that the crystallizer at any time is completely filled with suspension or melt. Therefore, explosible gas mixtures inside the crystallizer cannot be formed. In one side of the ring-crystallizer is placed the tube-bundle heat exchanger. The other side can be equipped with a cylindrical extension, if necessary for a sufficient retention time or to complete desupersaturation.

The heat exchanger of that system has to be operated incrustation-free over long periods, requiring a design which takes care for the driving-forces. The tendency towards formation of incrustations will be the less, as smaller the undercooling of melt or solution is chosen, resp. supersaturated. That concerns as well the supersaturation created inside the circulated suspension, as also especially the supersaturation which additionally is formed in the boundary layers on the cold heat exchanger surfaces.

The supersaturation in the circulated melt is kept smaller than the metastable field width /15/ and that is in the range of some g/l, only. With the strong temperature dependences of solubilities of the most organics this results in an undercooling of only some tenth degrees centigrade. With regard to incrustation behaviour the undercooling of the heat exchanger surfaces has to be minimized. Determination of the allowable value requires experimental work.

The heat exchanger is operated counter-currently, so that undercooling is kept constant over the full tube length. This requires a cooling water circuit of the same order as the internal circulation flow inside the crystallizer. The cooling water is added into this cooling water circuit.

The crystallization of bisphenol A - phenoladduct was realized in large-scale already some years ago. For the mechanical separation of the suspension are installed vertical peeler centrifuges. Because of the phenolic atmosphere the centrifuge is completely encapsuled and kept under nitrogen. Washing with phenol is possible.

The achieved product shows a mean crystal length of abt. 1 mm with thicknesses of 50 - 100 μm . Starting with a product impurity percentage of abt. 70 % the final product reaches a purity of more than 99 %, calculated as bisphenol A. The time periods between the cleanings at full load operation come up to 12 days. Cleaning, which is simply effected by heating the crystallizer content via an external heat exchanger, takes only one shift. The space-time-yield is 50 kg/m³ h. The specific crystallizer performance reaches 38 t/m² a and is by factor 4 larger than those of typical melt crystallizers.

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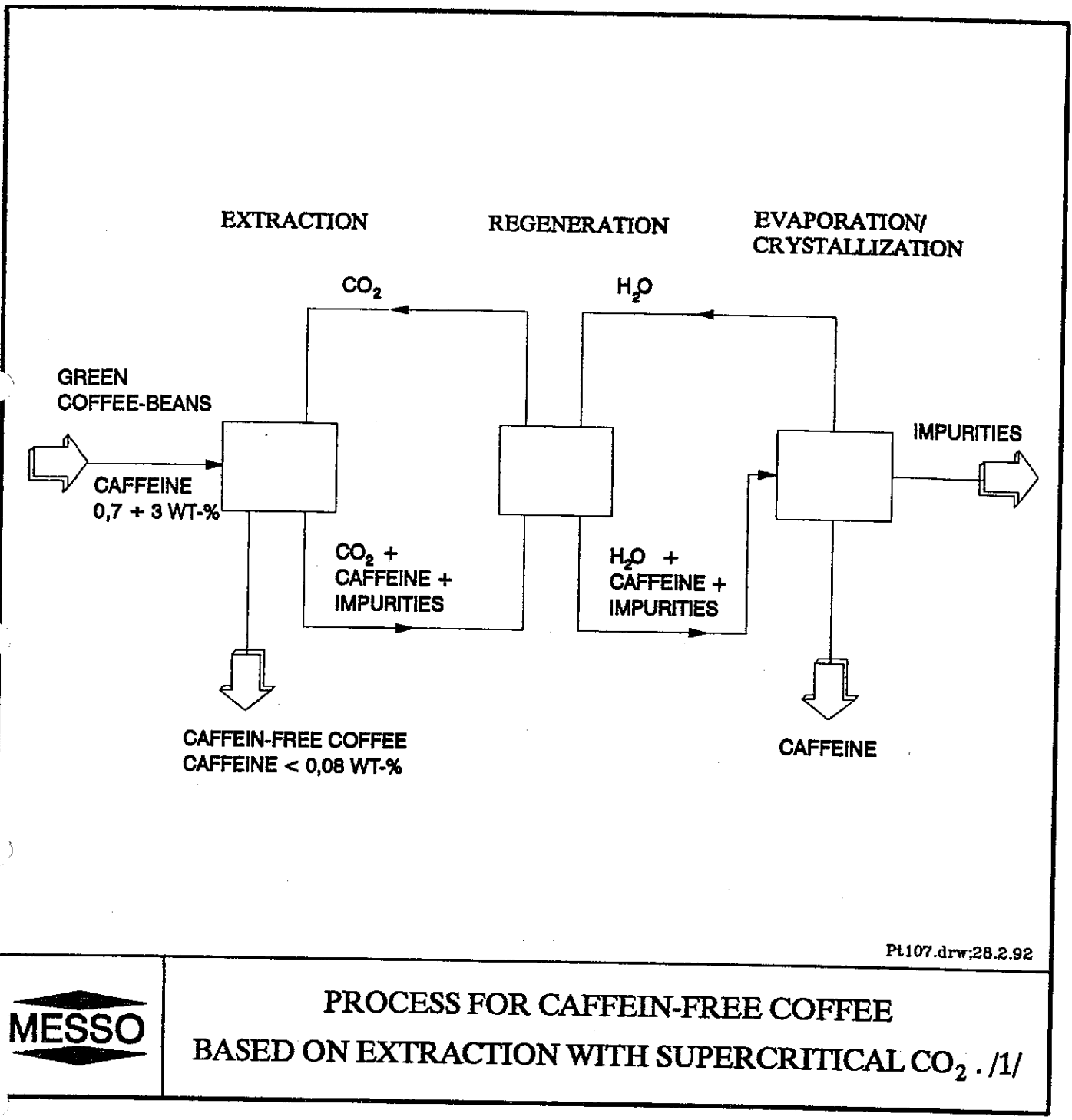


FIG. 1

COMPOSITION OF FEED SOLUTION:
(REGENERATION EFFLUENT)

CAFFEINE: 0,14 + 1 WT-%
SOLUTION/COFFEE MASS RATIO 3 + 5
COLOURED, SLIGHTLY TURBID LIQUOR

SPECIFICATION OF CAFFEINE
(ACC: TO INTERNATIONAL PHARMA STANDARDS)

DESCRIPTION: COLOURLESS POWDER, ODOURLESS, BITTER TASTE
PURITY: 98,5 ÷ 101,0 WT-%, ANHYDROUS
MELTING POINT: 235 + 237,5 °C
LOSS ON DRYING: < 0,5 WT-% AT 105 °C
HEAVY METALS: < 0,001 WT-% AS LEAD
ARSENIC: < 0,0003 WT-%
SOLUBILITY: 2,0 G ARE CLEAR AND COLOURLESS
DISSOLVABLE IN 100 ML WATER
0,3 G ARE CLEAR DISSOLVABLE IN
2 ML CHLOROFORM
pH-VALUE: 5,5 ÷ 6,5 (1 WT-% IN HYDROUS SOLUTION)

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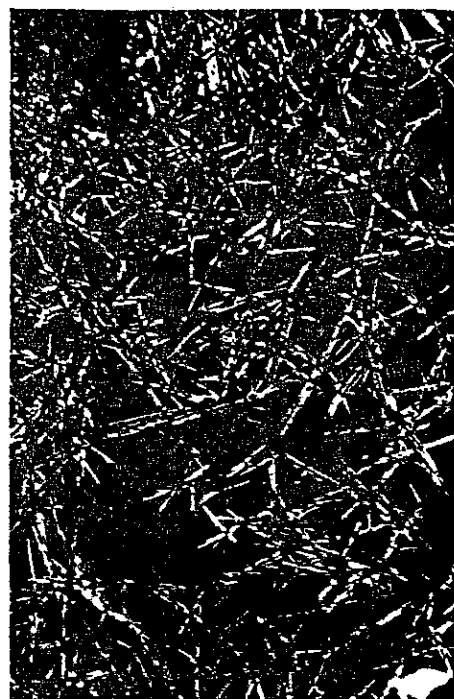
PROBLEM DEFINITION



**COMPACT PARTICLES,
ROD-SHAPED**



**POTATOE-SHAPED
CRYSTALS,
BROWNISH COLOUR**



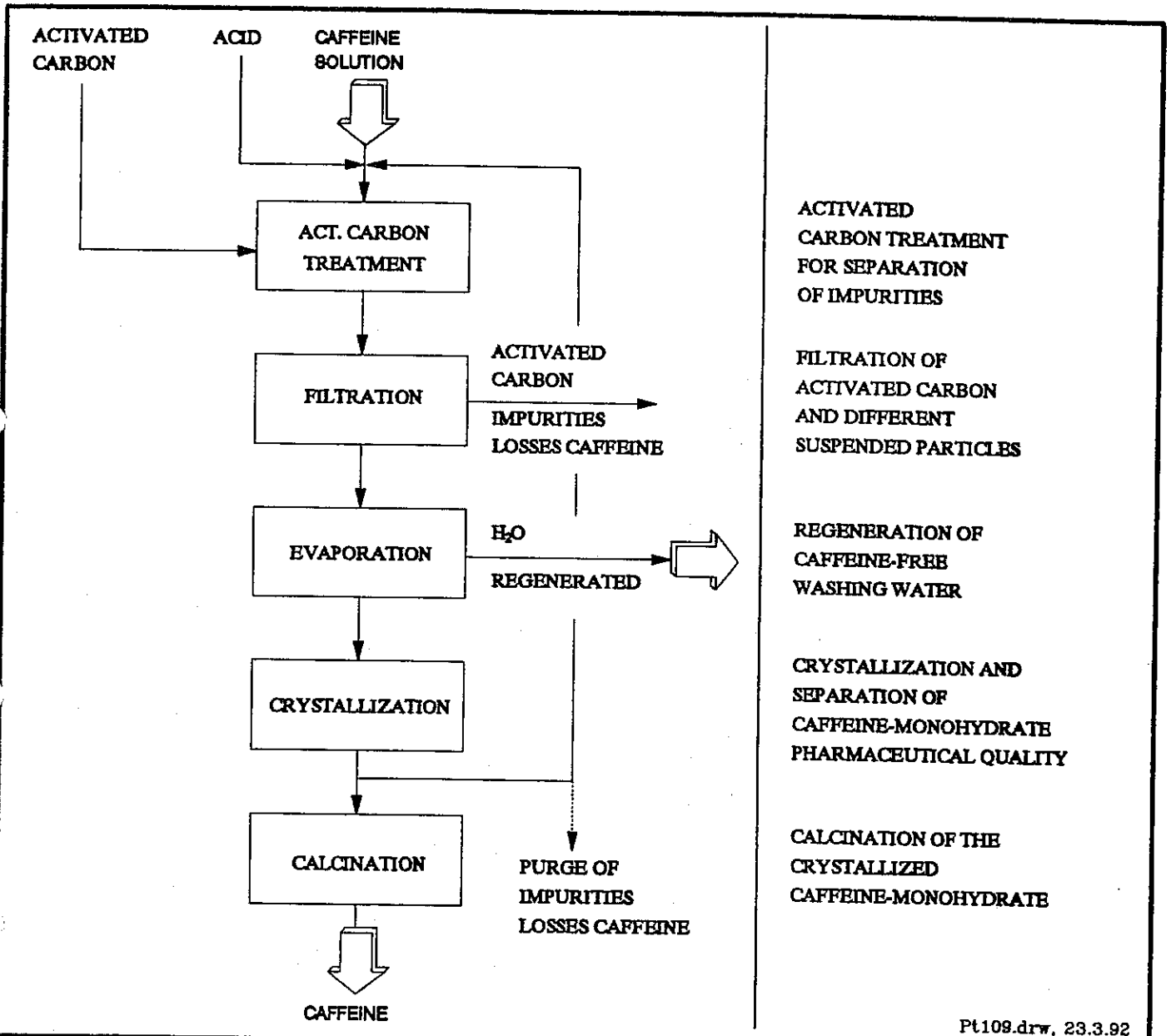
**FINAL PRODUCT
LONG, HAIRLIKE NEEDLES**

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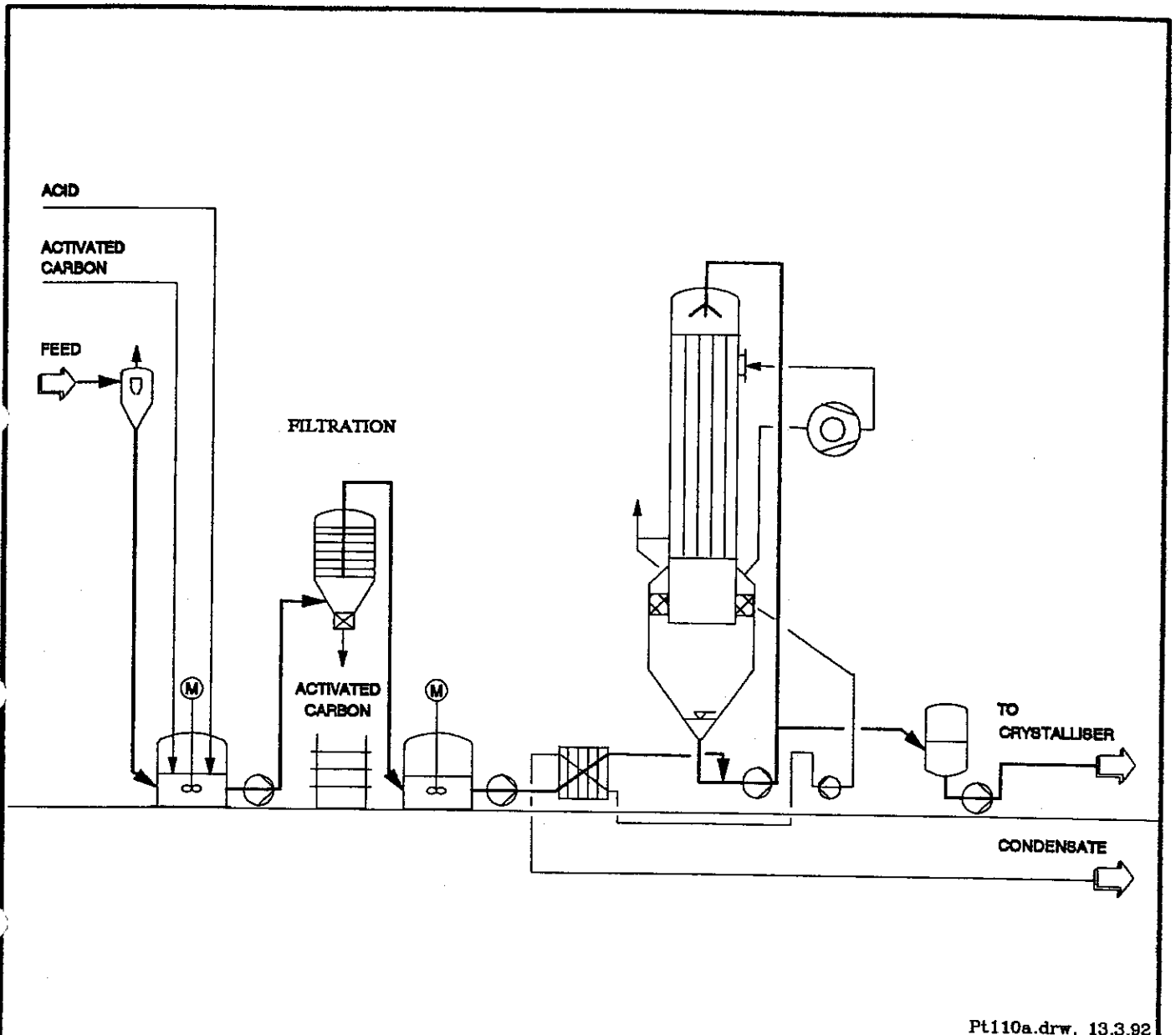
CAFFEINE CRYSTALS

FIG. 3



BLOCK FLOW SHEET CAFFEINE PREPARATION

FIG. 4

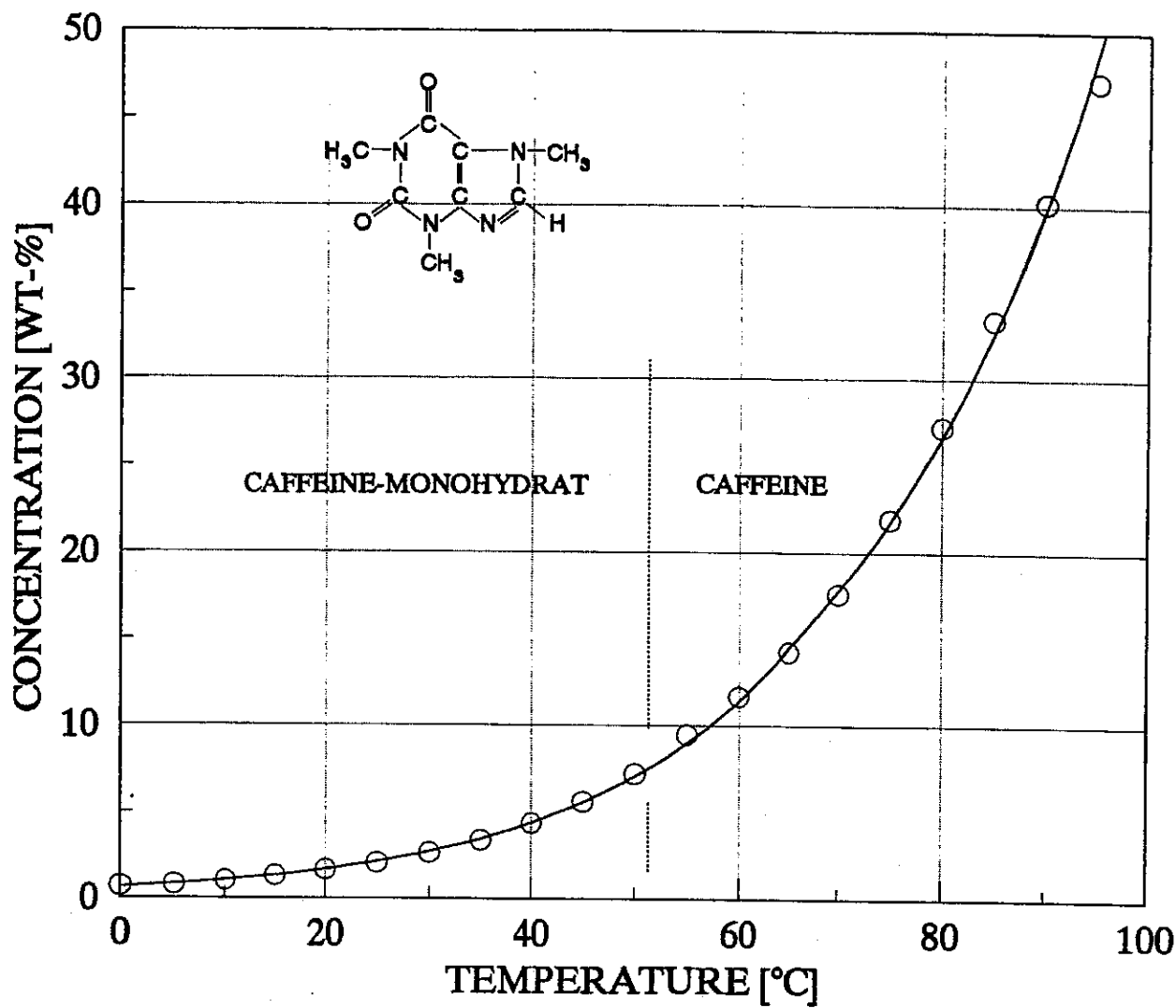


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**SIMPLIFIED FLOW SHEET FOR
SOLUTION PREPARATION**

FIG. 5



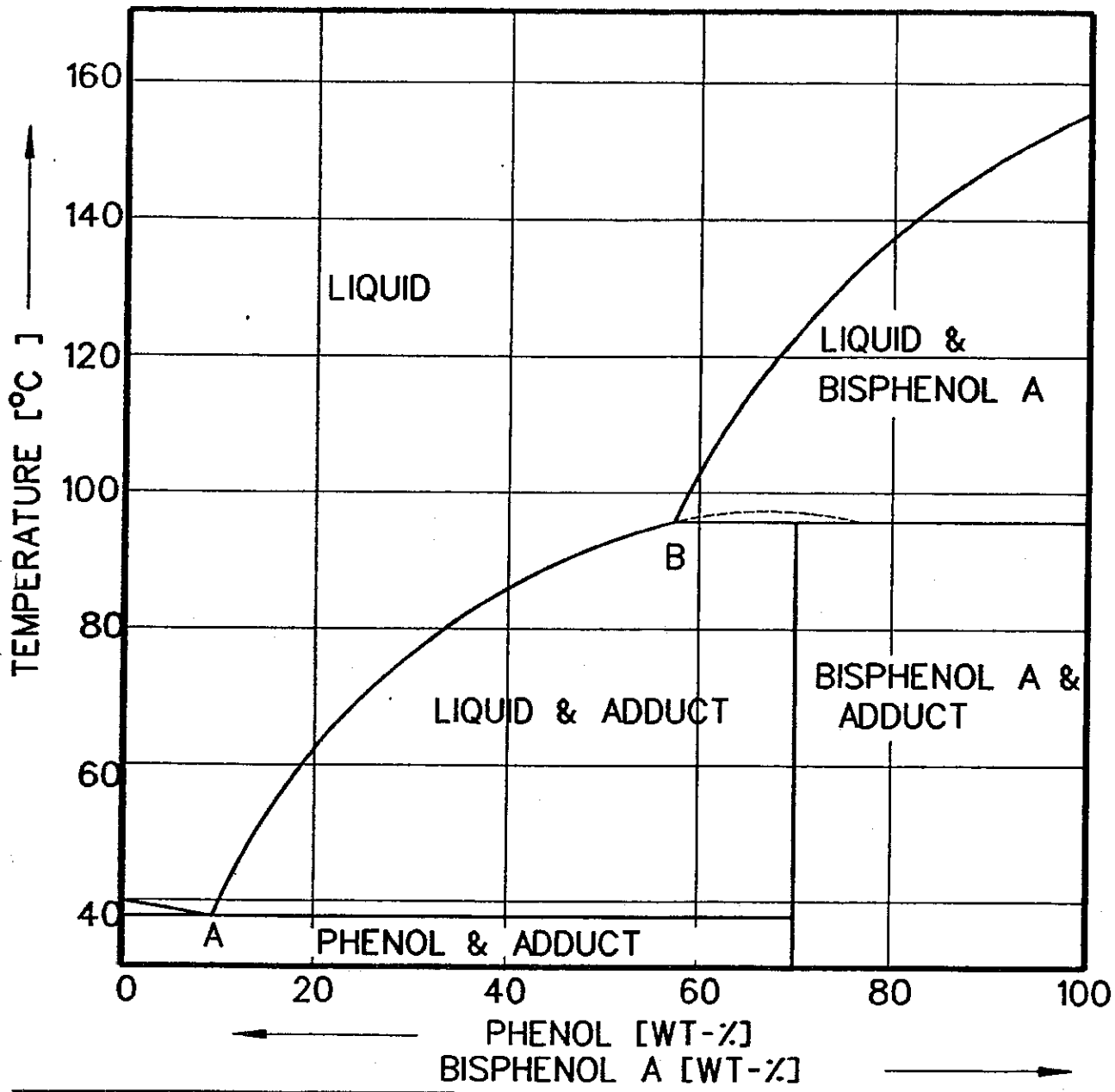
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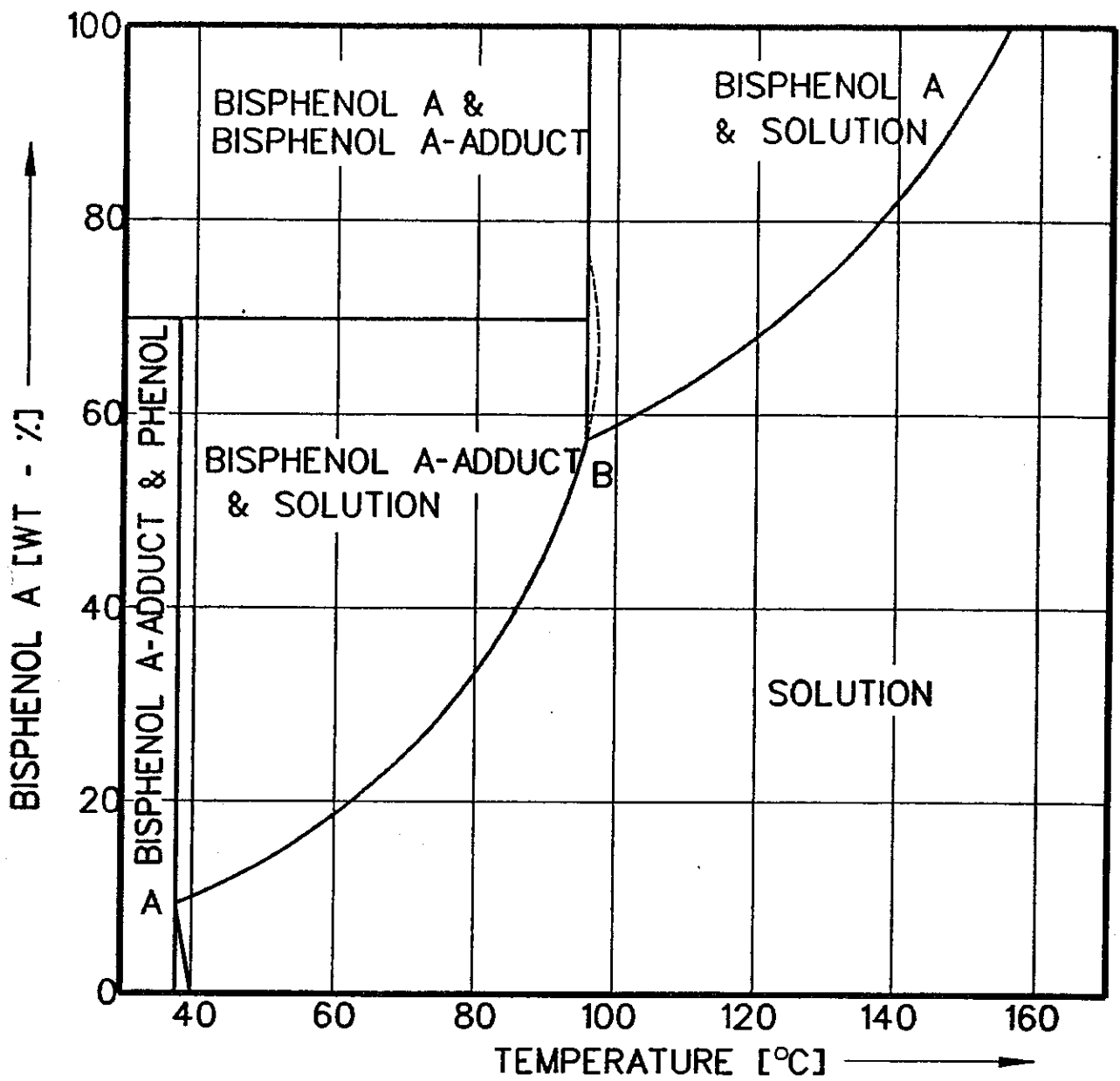
SOLUBILITY OF CAFFEINE IN WATER

FIG. 6



PHASE DIAGRAM
BISPHEENOL A - PHENOL

FIG. 7



SOLUBILITY DIAGRAM
BISPHENOL A - PHENOL

FIG. 8

COOLING/HEATING
MEDIUM

COOLING/HEATING
MEDIUM

MELT

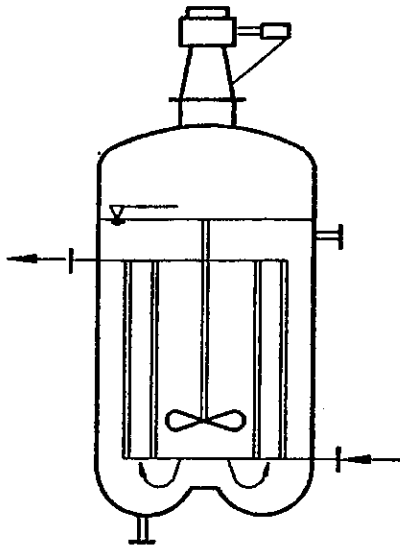
CIRCULATION

RESIDUE/
PURE PRODUCT

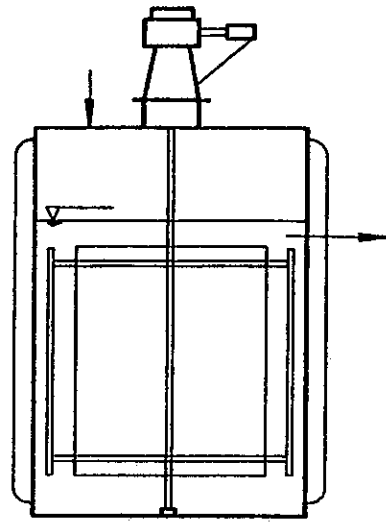
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FALLING FILM - CRYSTALLIZER

FIG. 9



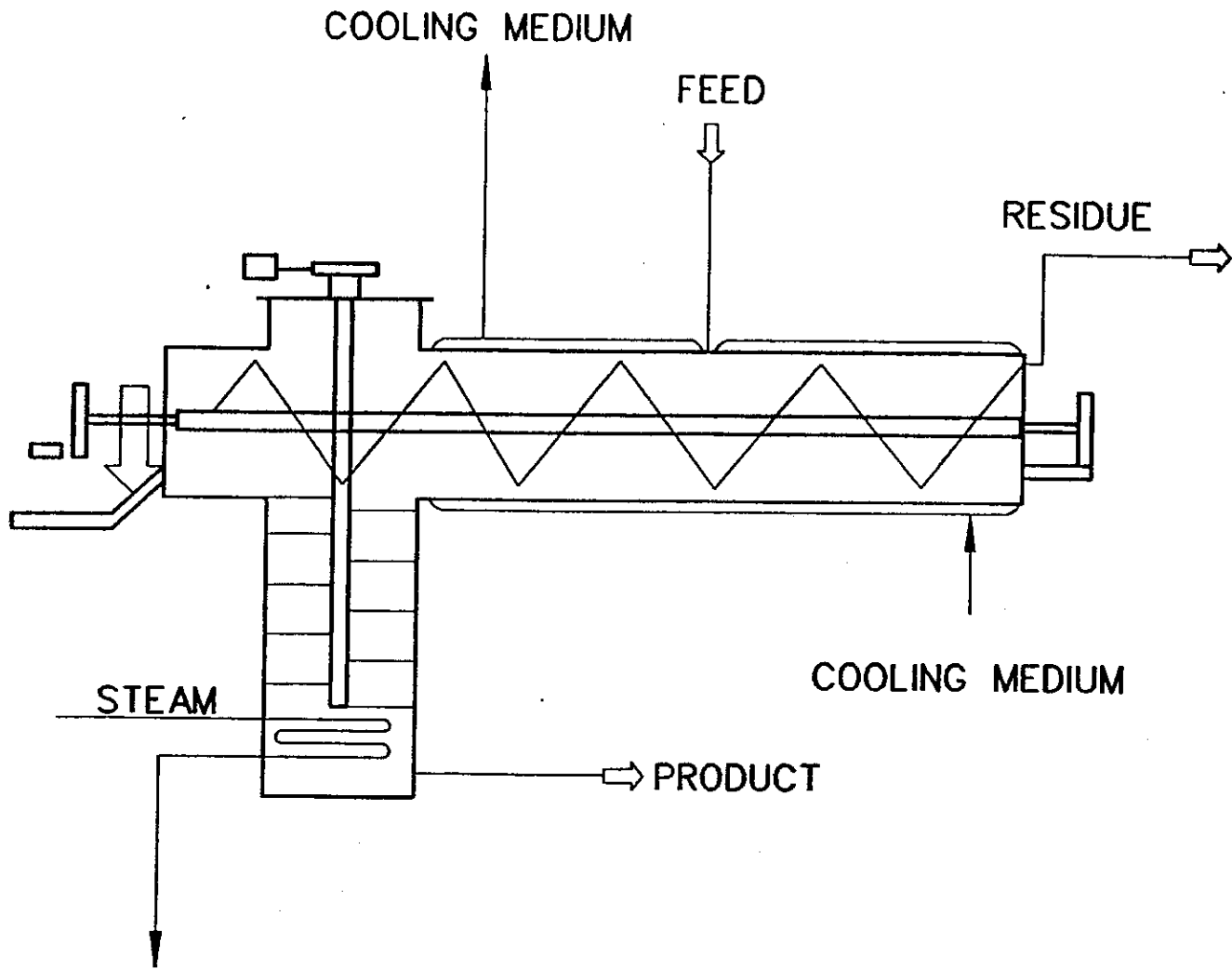
WITH COOLING ELEMENTS



AS SCRAPED REFRIGERATOR

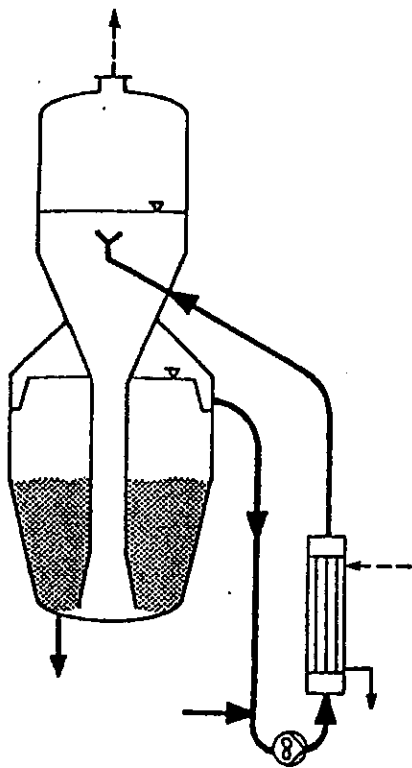


MELT CRYSTALLIZERS
AGITATING TANK, INDIRECT COOLED



BRODIE PURIFIER

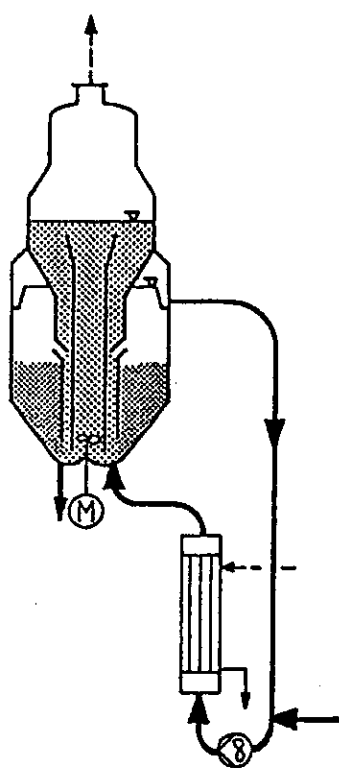
FIG. 11



OSLO-
CRYSTALLIZER

$d' > 1,5 \text{ mm}$

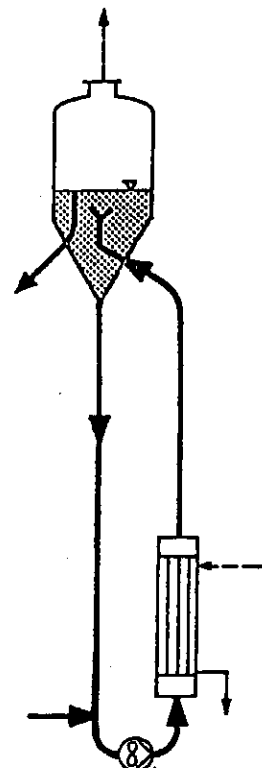
$n > 4,0$



DRAFT TUBE
CRYSTALLIZER

$d' \approx 0,5-1,5 \text{ mm}$

$n = 2,5-4,0$



FC-
CRYSTALLIZER

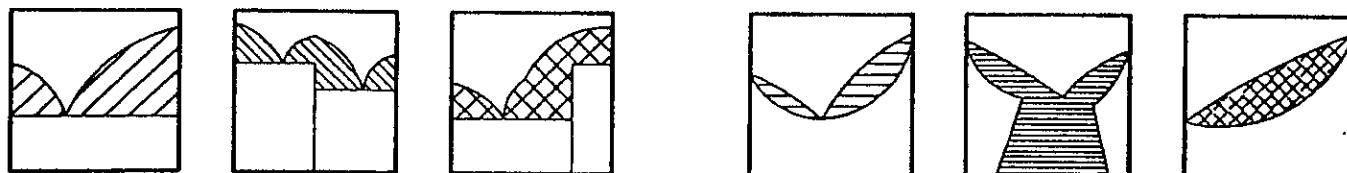
$d' \approx 0,2-0,6 \text{ mm}$

$n = 2-2,5$

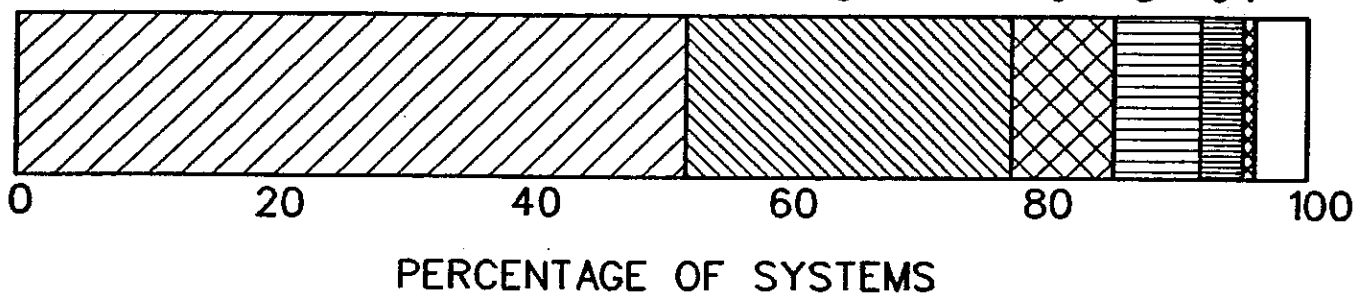
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TYPES OF CRYSTALLIZERS

FIG. 12



- a - EUTECTIC SYSTEM
- b - SYSTEM WITH CONGRUENT MOLTEN COMPOUND
- c - PERITECTIC SYSTEM
- d - AZEOTROPIC SYSTEM WITH UNLIMITED SOLID SOLUTION
- e - EUTECTIC SYSTEM WITH LIMITED SOLID SOLUTION
- f - IDEAL SYSTEM



TYPICAL PHASE DIAGRAMS OF
BINARY ORGANIC SYSTEMS

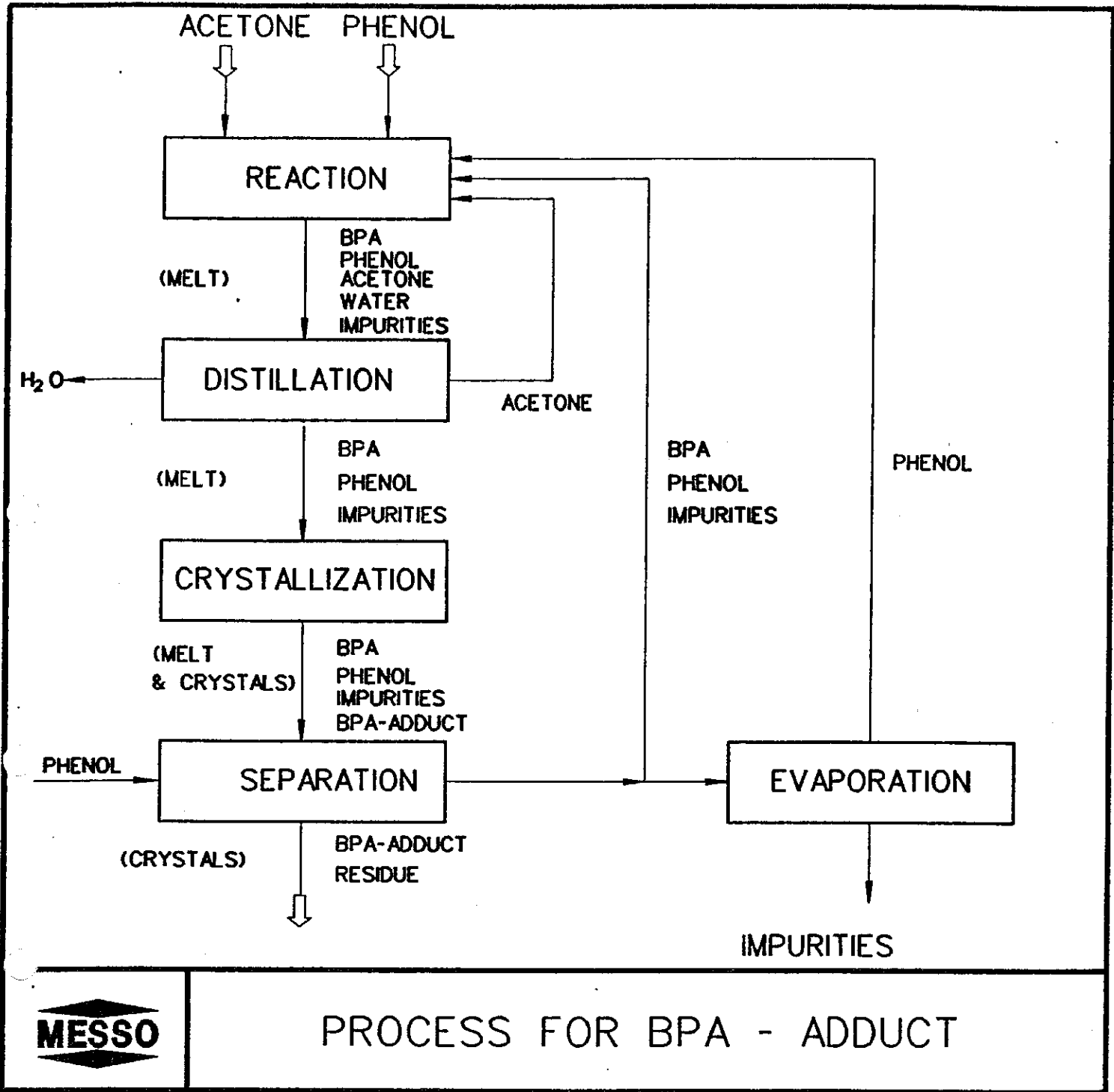
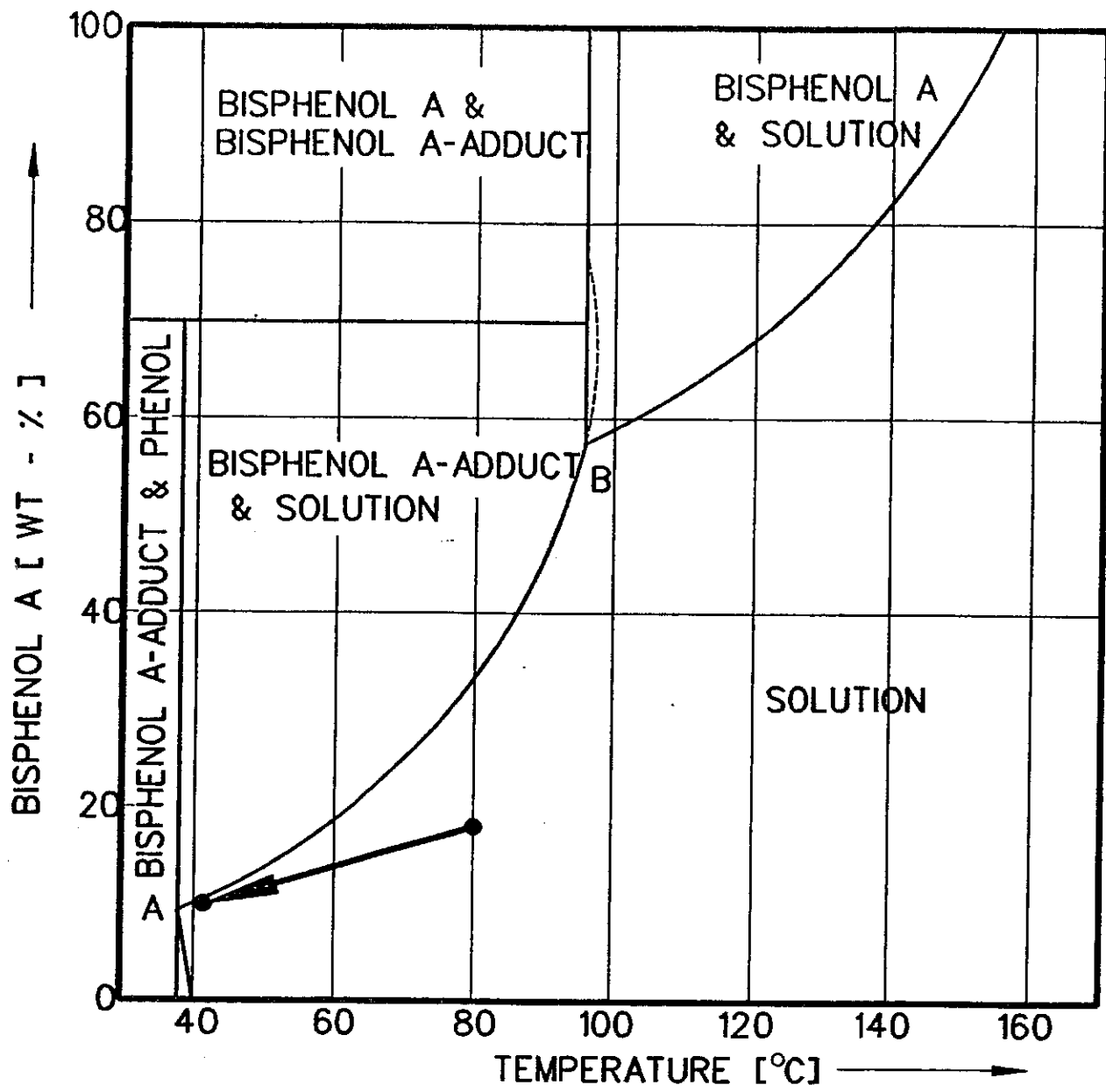
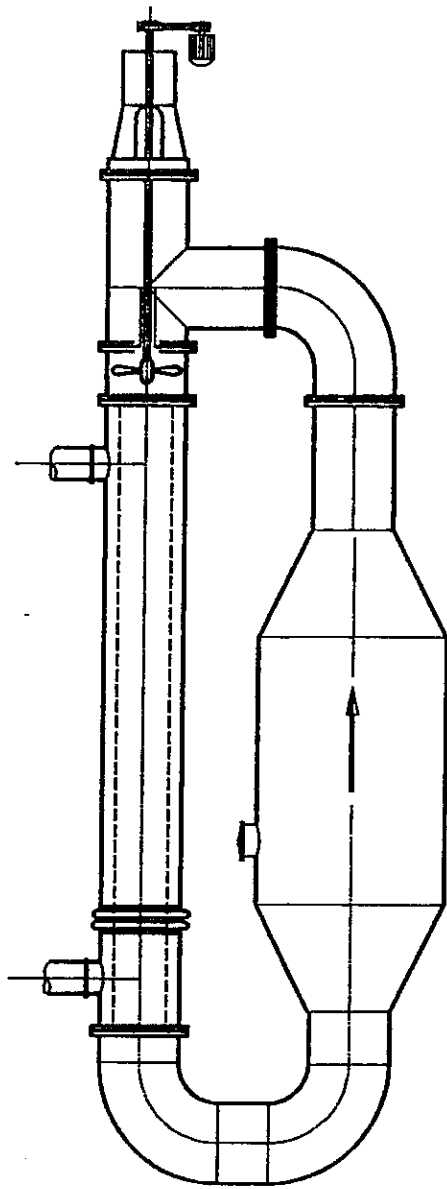


FIG. 14



SOLUBILITY DIAGRAM
BISPHENOL A - PHENOL

FIG. 15



MESSO

LOOP CRYSTALLIZER

FIG. 16