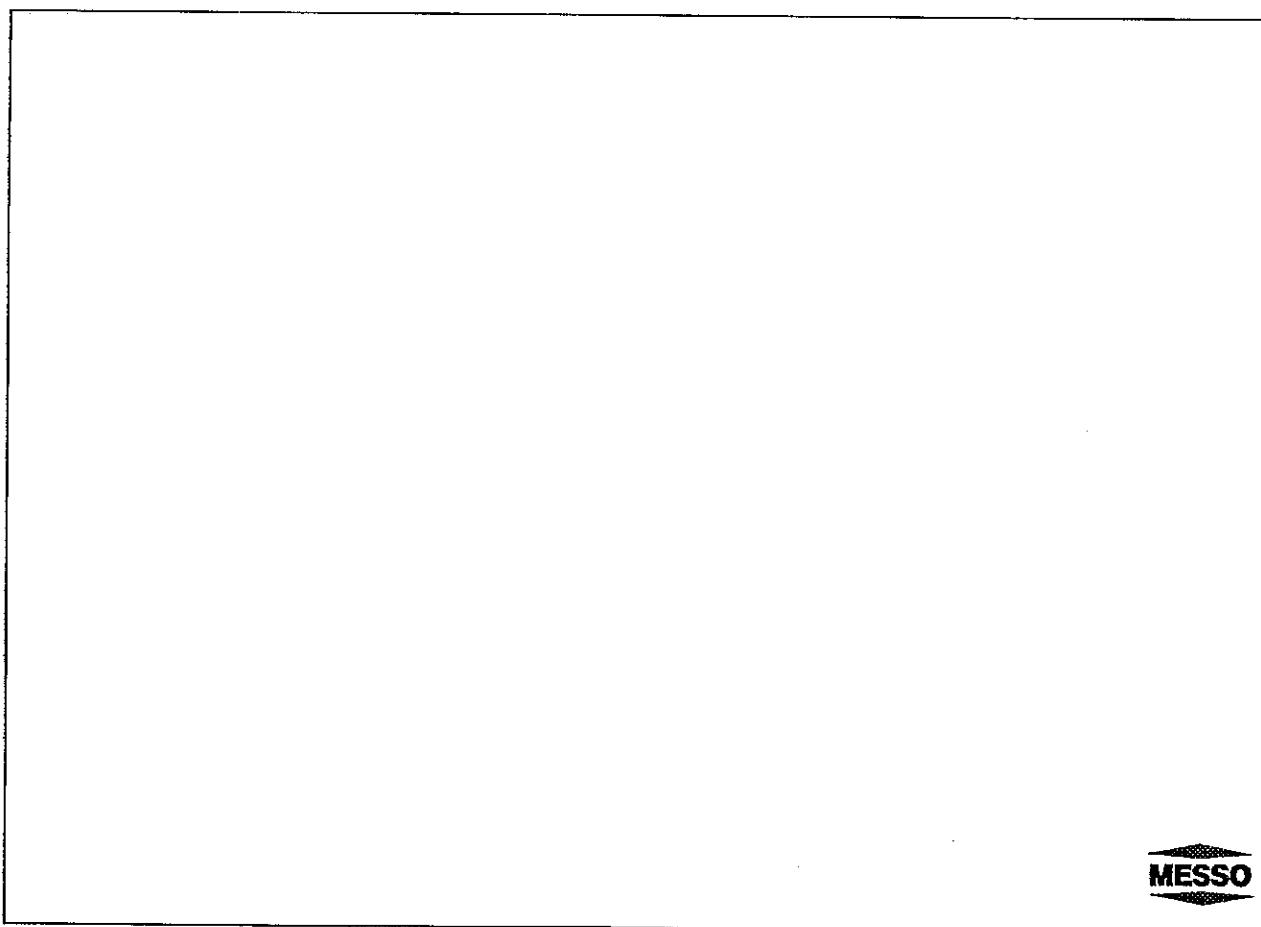


Recovery of Caffeine in Decaffeination Using Supercritical Carbon Dioxide

Günter Hofmann, H. D. Kutta



RECOVERY OF CAFFEINE IN DECAFFEINATION USING SUPERCRITICAL CARBON DIOXIDE

G.Hofmann, H.D.Kutta

MESSO - CHEMIETECHNIK GmbH

Friedrich-Ebert-Straße 134

D 4100 Duisburg 14

1 New decaffeination process

A new development typical for the today's requirements in the field of mass crystallization is the industrial production of caffeine in pharmaceutical quality from the new decaffeination process with supercritical carbon dioxide.

The conventional technology for decaffeinating 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 effective 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]. The CO₂ used is taken from air, i.e. not influencing the environment's CO₂ balance 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 decaffeinating 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 with water. Whereas the regenerated carbon dioxide is recycled, the caffeine-containing wash water has to be

withdrawn. The caffeine concentration in this used wash water is extremely low. It is maintained at the level of only 1.4 to 10 g/l [1], otherwise the caffeine concentration in the beans could not be reduced to the necessary target. As a consequence, the consumption of fresh water is quite high (3 to 5 kg/h per kg green coffee).

Fresh water must be prepared before use to keep the coffee 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 the valuable pharmaceutical quality, for which only the natural caffeine is approved. Consequently, the appropriate recovery of caffeine becomes the key for decaffeination using CO₂.

The process requirements are given by the wash water composition and the specification for the pharmaceutical caffeine quality (Fig. 2). Beside some turbid solid impurities which appear to be some kind of waxes, the wash waters are quite pure, although obviously containing traces of strong coloured components beside caffeine. On the very first view it appears clear the process has to consist of a water recovery and a crystallization step, at least.

In addition to crystallization, however, some other unit operations had to be introduced to meet the product specification finally. It demonstrates how strong the presence of minor impurities can influence the design of industrial crystallization processes. The development of such a process requires at first the knowledge of crystallization's possibilities and its limitations at the same time.

2 Lab investigations for the isolation of caffeine

For the development of this process at 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 caffeine specification by crystallization was found to be definitely more complicate. Caffeine is known to crystallize in two modifications, the anhydrite and a monohydrate. The transient point is not exactly analysed, but lies somewhere between 50 and 70 °C. Crystals are reported to be extremely long matted together and forming hairlike needles (right photo in Fig. 3) [2]. In opposite to this our first products however, showed compact particles, rod-shaped and sometimes also like potatoes with a brownish colour (left and center, Fig. 3). Even with recrystallization and charcoal treatment it was impossible to reach the required whiteness quality. In any other respects these samples already met the pharmaceutical quality

Obviously, the incorporated coloured impurities took strong influence to the crystal shape, either as strong habit modifiers or as perhaps some kind of mixed crystals, leading to completely different crystal shapes.

Some decomposition of caffeine was recognized to be responsible for the presence of these coloured impurities. Fig. 4 shows the increase of extinction with concentration we observed, indicating a certain formation of coloured components during evaporation, which we found to be only slightly dependent on temperature. Oxidation by air oxygen was isolated to be mainly responsible for this behaviour, leading immediately to dark brown liquors, when air was re-contacting solutions after the vacuum evaporation. That is indicated in Fig. 5 by the remarkable increase of extinctions in that liquors, which were exposed to air over night. Literature reports hydrolytic decomposition into caffeidine dicarbonic acid and/or 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. Fig. 6 points out the reduced formation of coloured substances during evaporation with lowering the pH. Decomposition by oxidation was depressed.

After treatment of these acidified solutions with activated carbon - that acidification enforces the adsorption behaviour of activated carbon was a lucky coincidence - caffeine of pharmaceutical quality could be produced for the first time.

But, as can be seen from the photo of the final product in Fig. 3 (right), this time the crystal shape was that known from literature, i.e. very long hairs, rather than hairlike needles, especially, if crystallization was done in unstirred solution by cooling over night, pointing out the natural impurity to be a very effective habit modifier.

The CSD of the achieved products is hardly to describe. The mean crystal size could be characterized with abt. 20 microns thickness and 200 microns length. But, as the final calcination to anhydrite changes the product size anyway the deciding figure for the crystallizer design was the resulting separation efficiency of these fine products.

Filtration and washing remained troubleless for any of these qualities. All these crystals showed an excellent filtration and washing behaviour, so that the particle size was found out to be completely unimportant.

3 The resulting caffeine refining process

Consequently, the resulting process became assembled by the process steps (Fig. 7):

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

A plant design is presented in (Fig. 8). The caffeine-containing wash water entering the plant at first is slightly expanded, allowing the remaining carbon dioxide leaving with the vapours. Activated carbon powder is added to the solution after lowering the pH. After adsorption the suspension is separated, the sludge wasted and the purified liquor given to evaporation. This example shows a conception consisting of a falling-film evaporation with mechanical vapour re-compression together with 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. 9). 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 this very low production capacities of only some kilograms.

The cooling has to be carried out at a quite low temperature to minimize product losses with the process 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 explained before, because the solution is already purified by the process steps before crystallization.

Thus, also the crystallizer (Fig. 10) 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. In opposite to this the circulation is enforced to keep these crystals suspended. The hairlike, tiny crystals are broken down anyway and afterwards also the crystallized caffeine monohydrate loses its shape during the calcination to the required anhydrite.

4 Experiences with the large-scale unit

A first large-scale plant was set into operation in 1991. The falling-film evaporation works without any fouling and the operation period for the continuous surface-cooled crystallizer between two washings reaches two weeks. The quality of the caffeine produced has fulfilled the market demands already since the very beginning.

Coming back to the remarkable effect on the crystal habit observed, for which some minor, perhaps only traces of impurities seem to be responsible, it should be pointed out that a more detailed study of this system could be of interest for an improved understanding of the habit modification principles.

5 Literature

1. Zosel, Kurt
Praktische Anwendungen der Stofftrennung mit überkritischen Gasen
Angew. Chemie 90 (1978), S. 748/755
2. United States Pharmacopeia XIX, p. 59
3. DAB 9, comments, p. 1304 - 1310

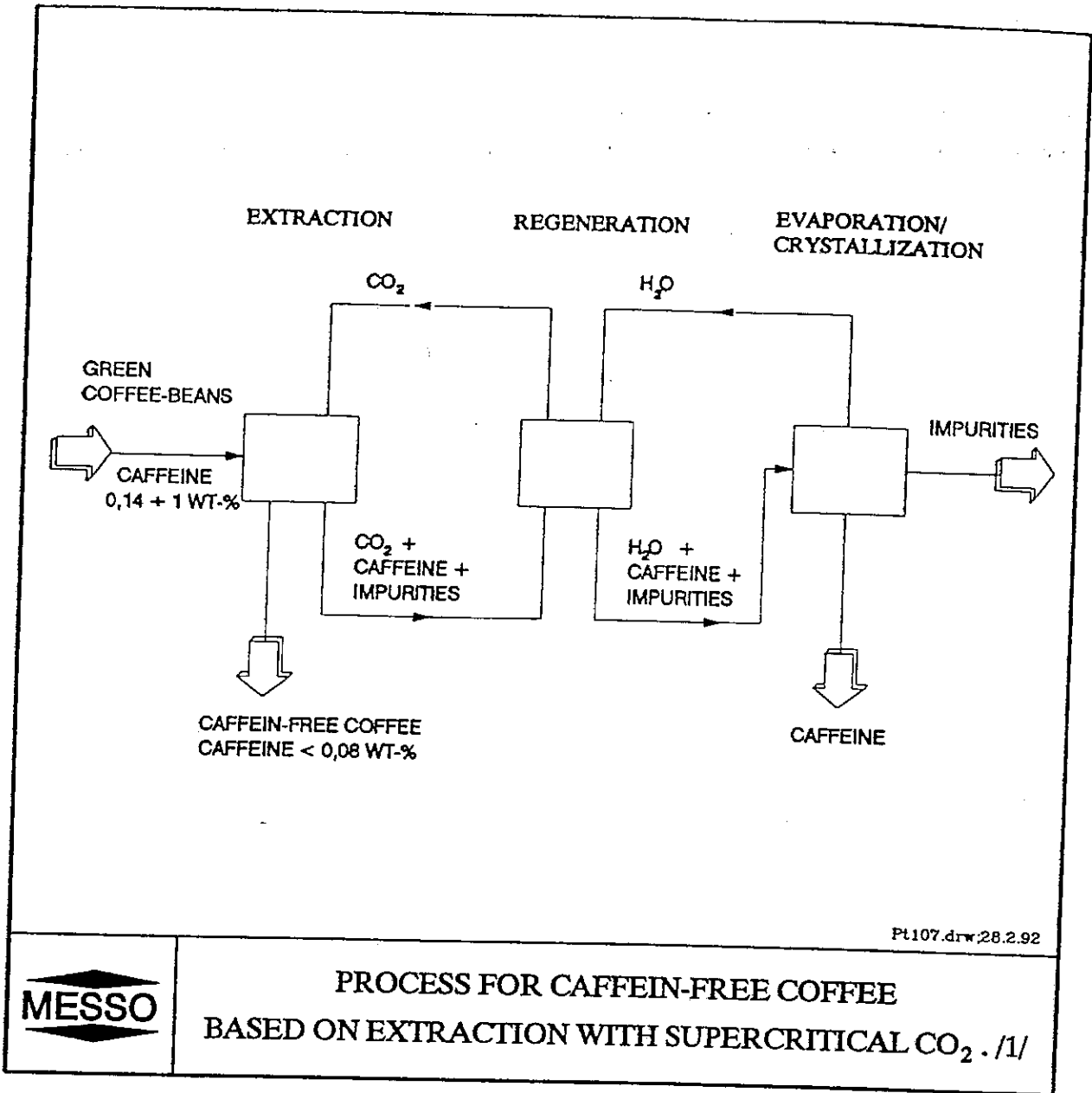


Fig. 1

**COMPOSITION OF FEED SOLUTION:
(REGENERATION EFFLUENT)**

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

SPECIFICATION OF CAFFEINE

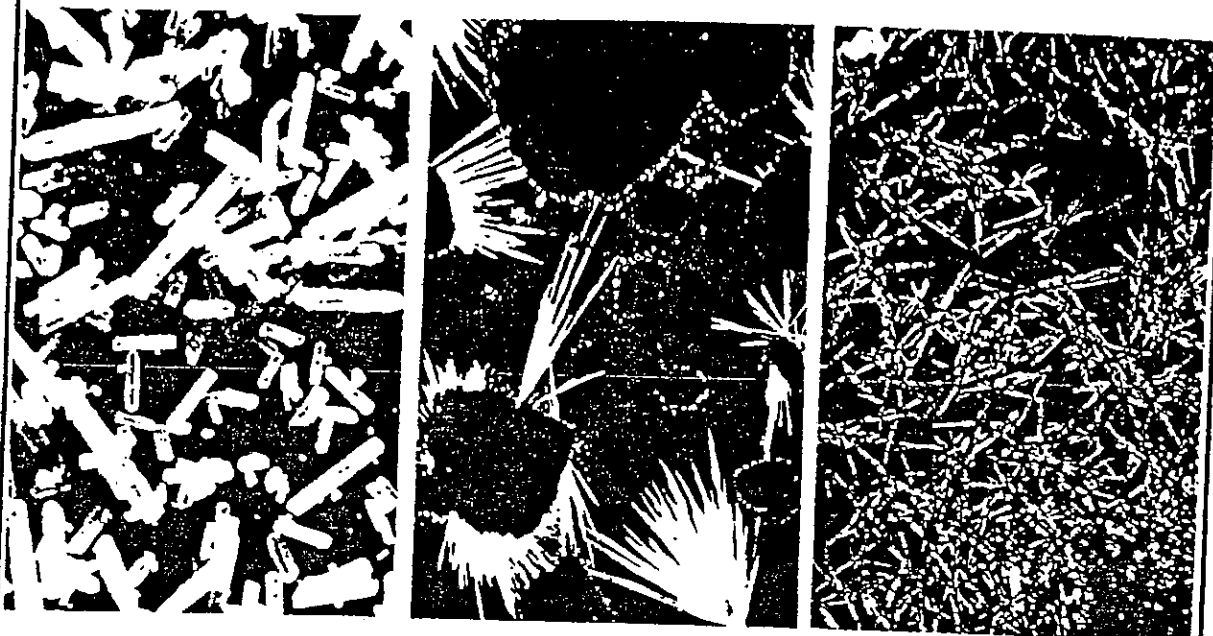
(ACC: TO INTERNATIONAL PHARMA STANDARDS)

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)

Pt108.drw. 23.3.92



PROBLEM DEFINITION



COMPACT PARTICLES,
ROD-SHAPED

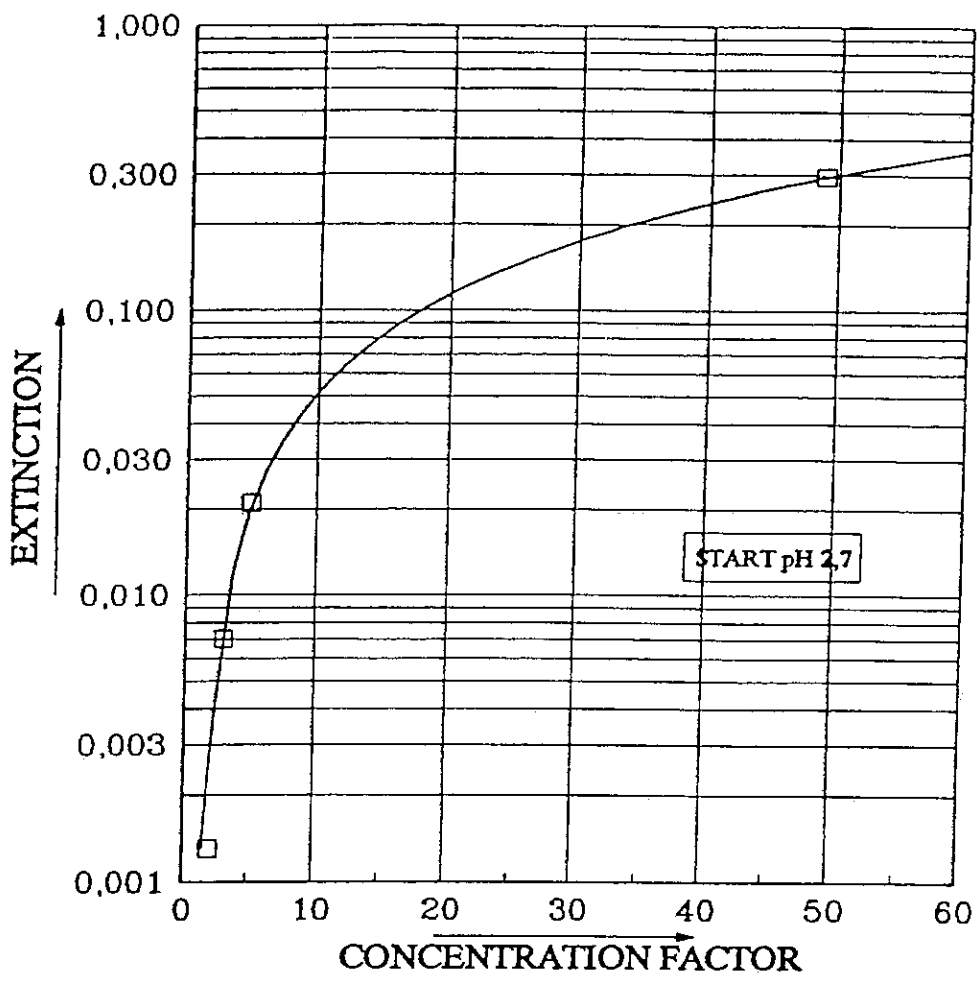
POTATOE-SHAPED
CRYSTALS,
BROWNISH COLOUR

FINAL PRODUCT
LONG, HAIRLIKE NEEDLES

Pt111.drw, 23.3.02

MESSO

CAFFEINE CRYSTALS



CUM-4-97/101



**EXTINCTION OF CONCENTRATES
AFTER EVAPORATION**

TRIAL NO. C 12.0

Fig. 4

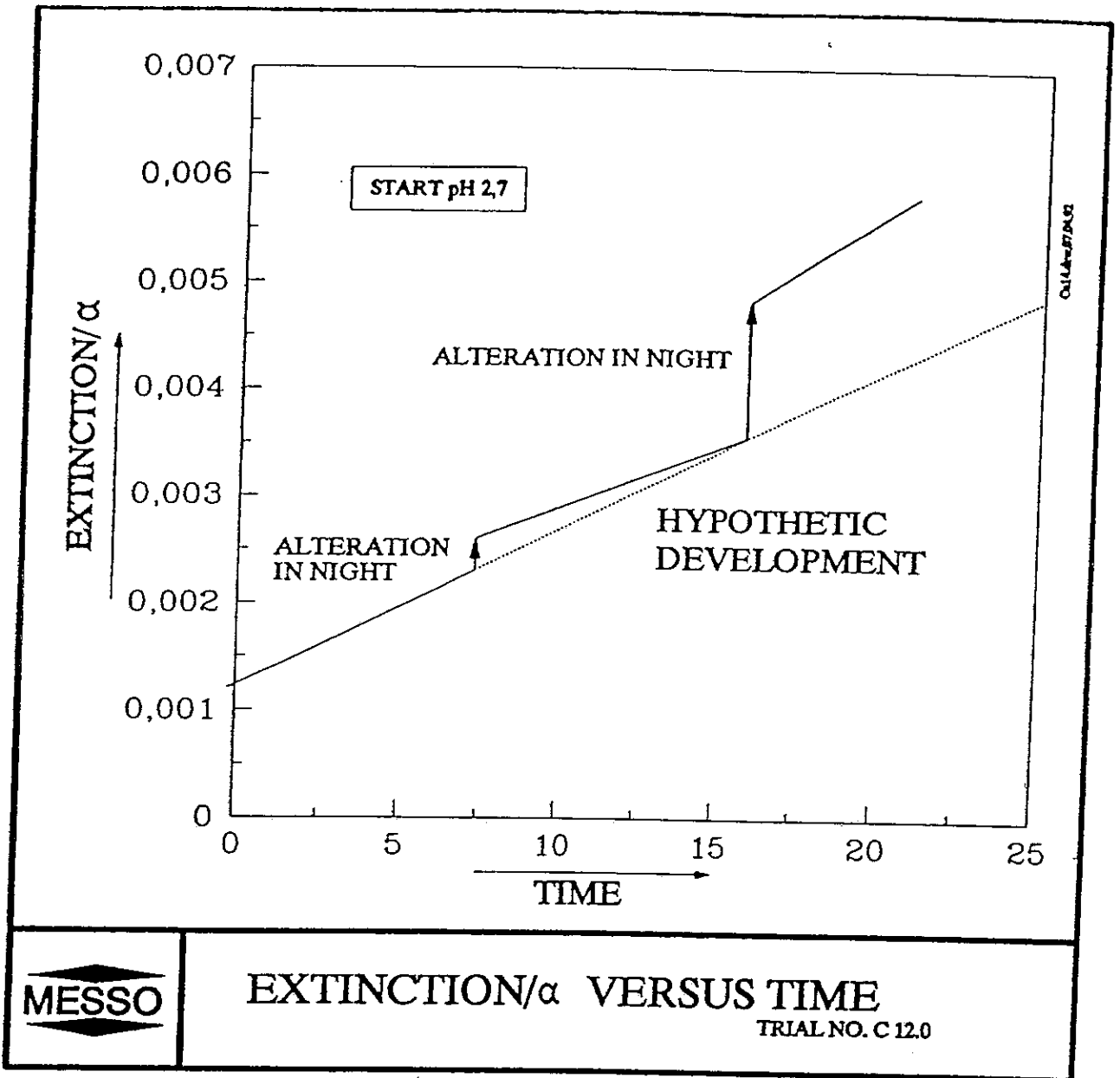
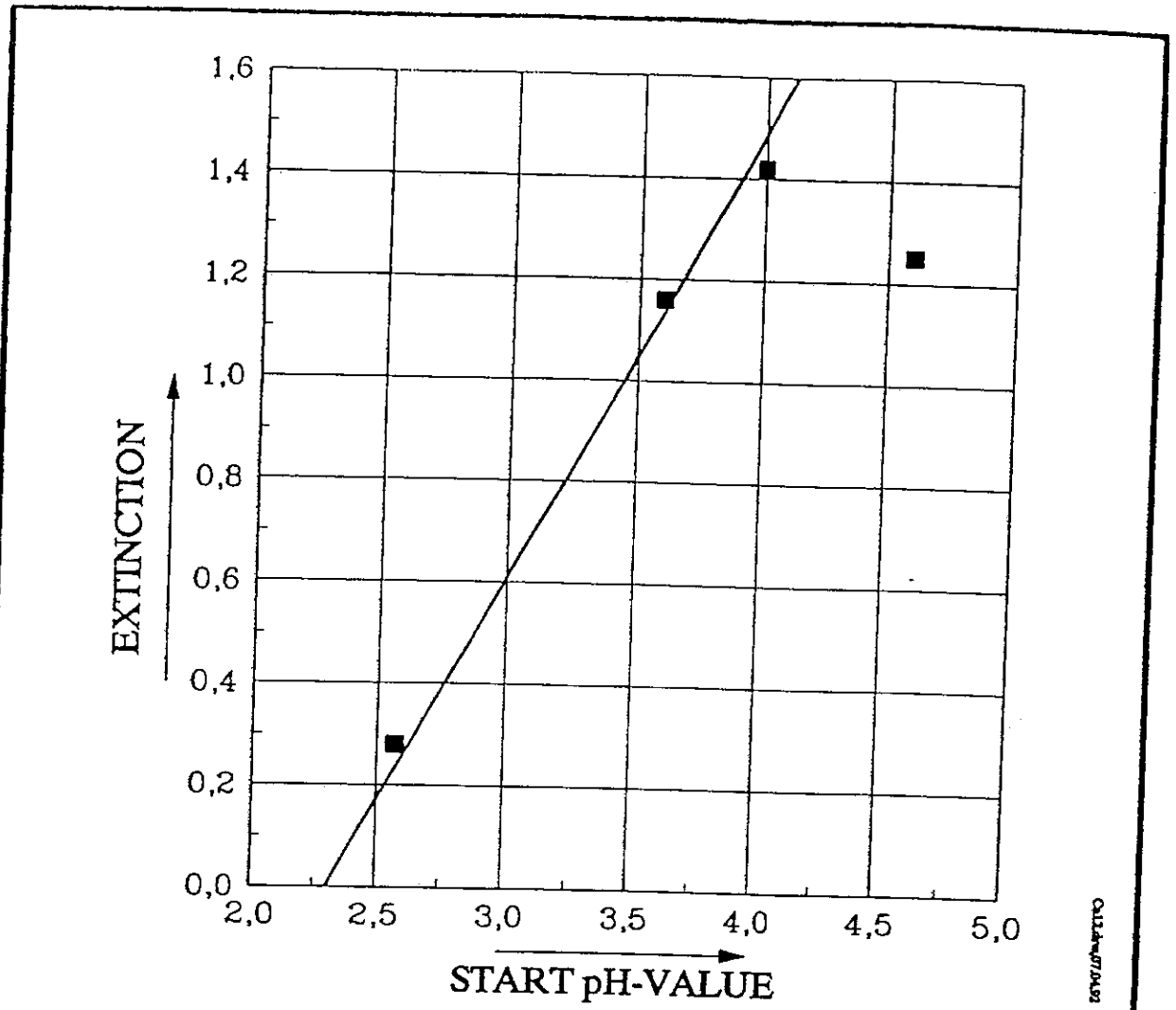


Fig. 5



EXTINCTION OF CONCENTRATES AFTER
DECOLOURIZATION AT DIFFERENT pH-VALUES

Fig. 6

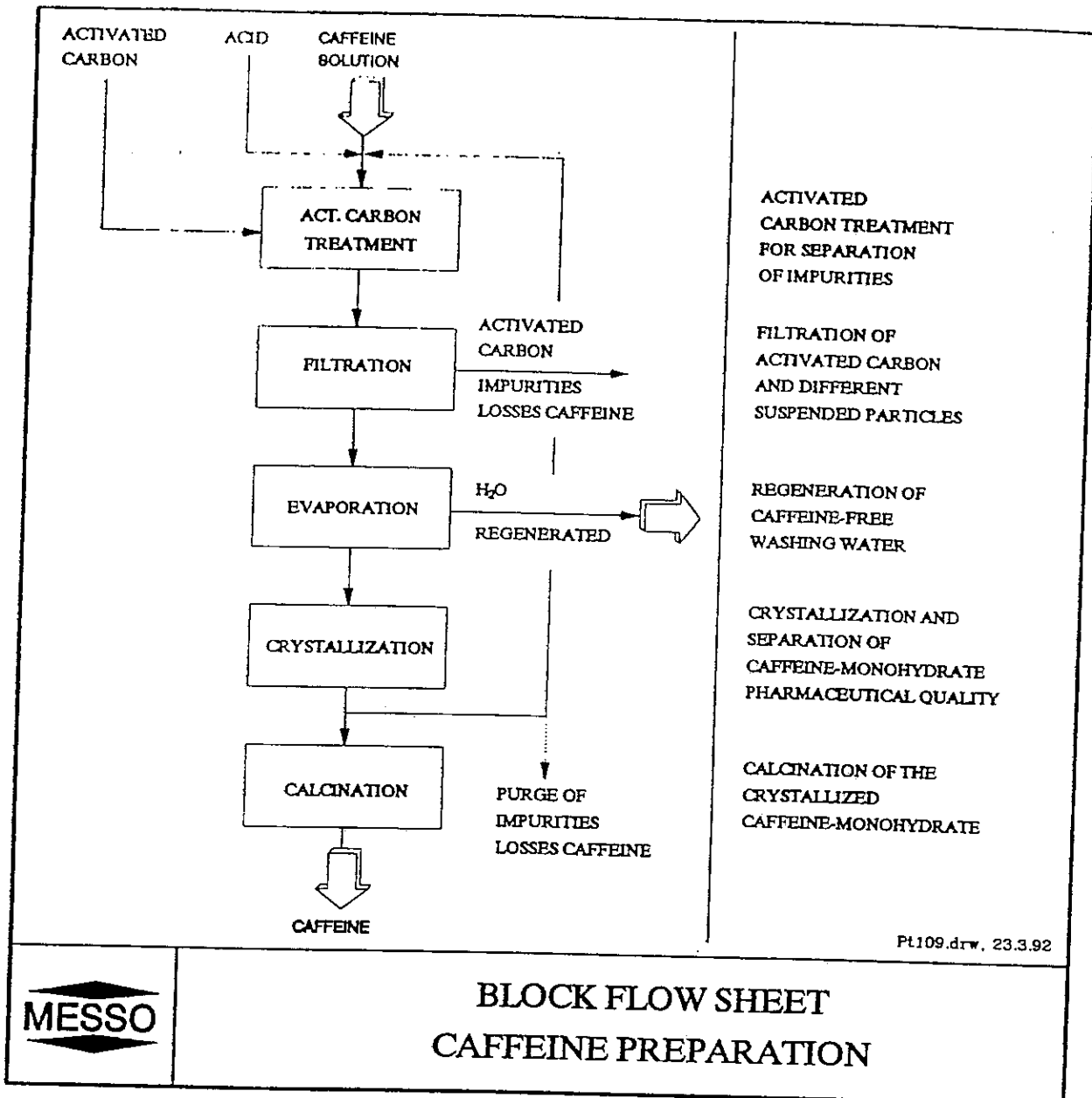
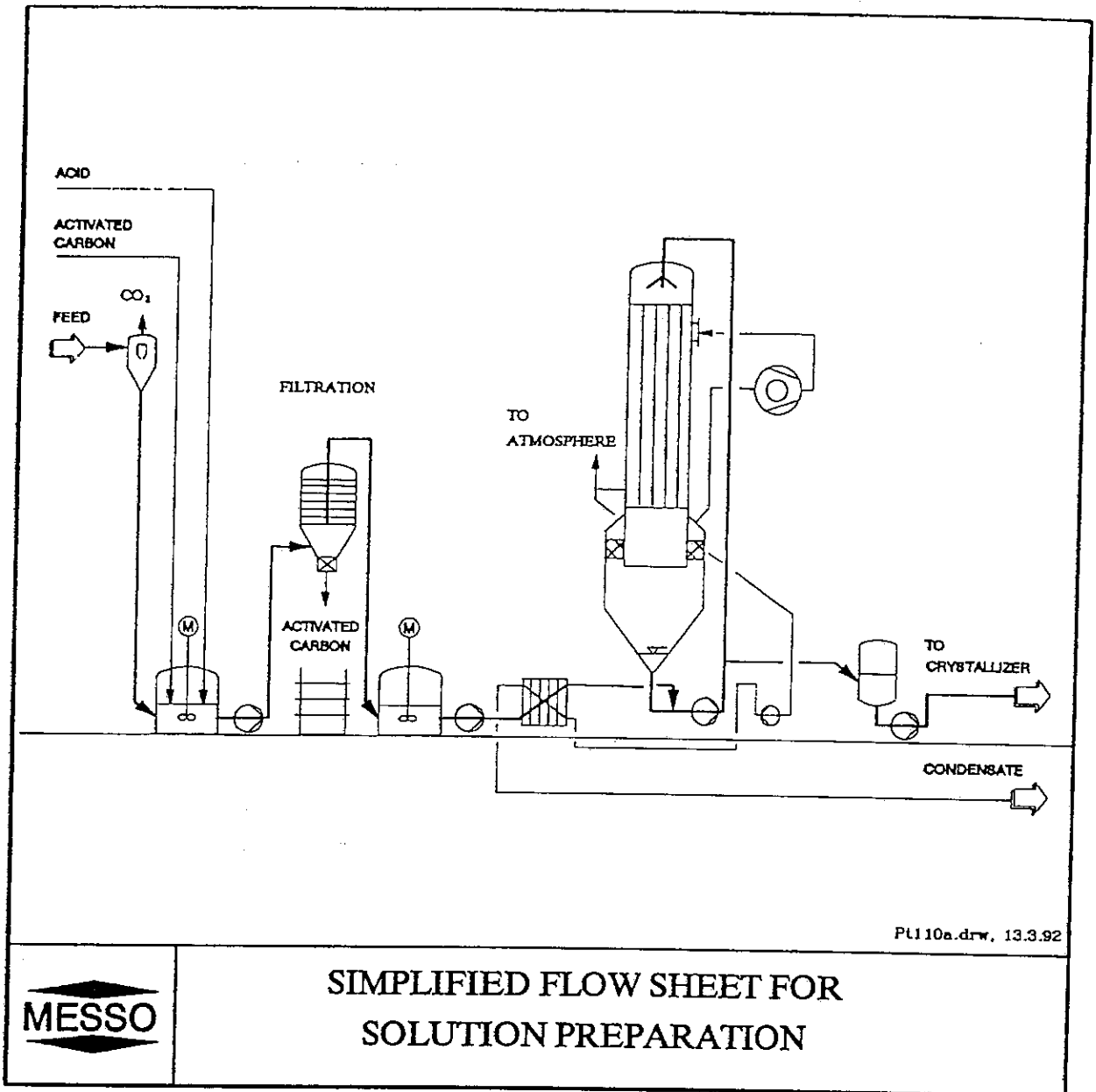


Fig. 7



PL110a.drw, 13.3.92



SIMPLIFIED FLOW SHEET FOR
SOLUTION PREPARATION

Fig. 8

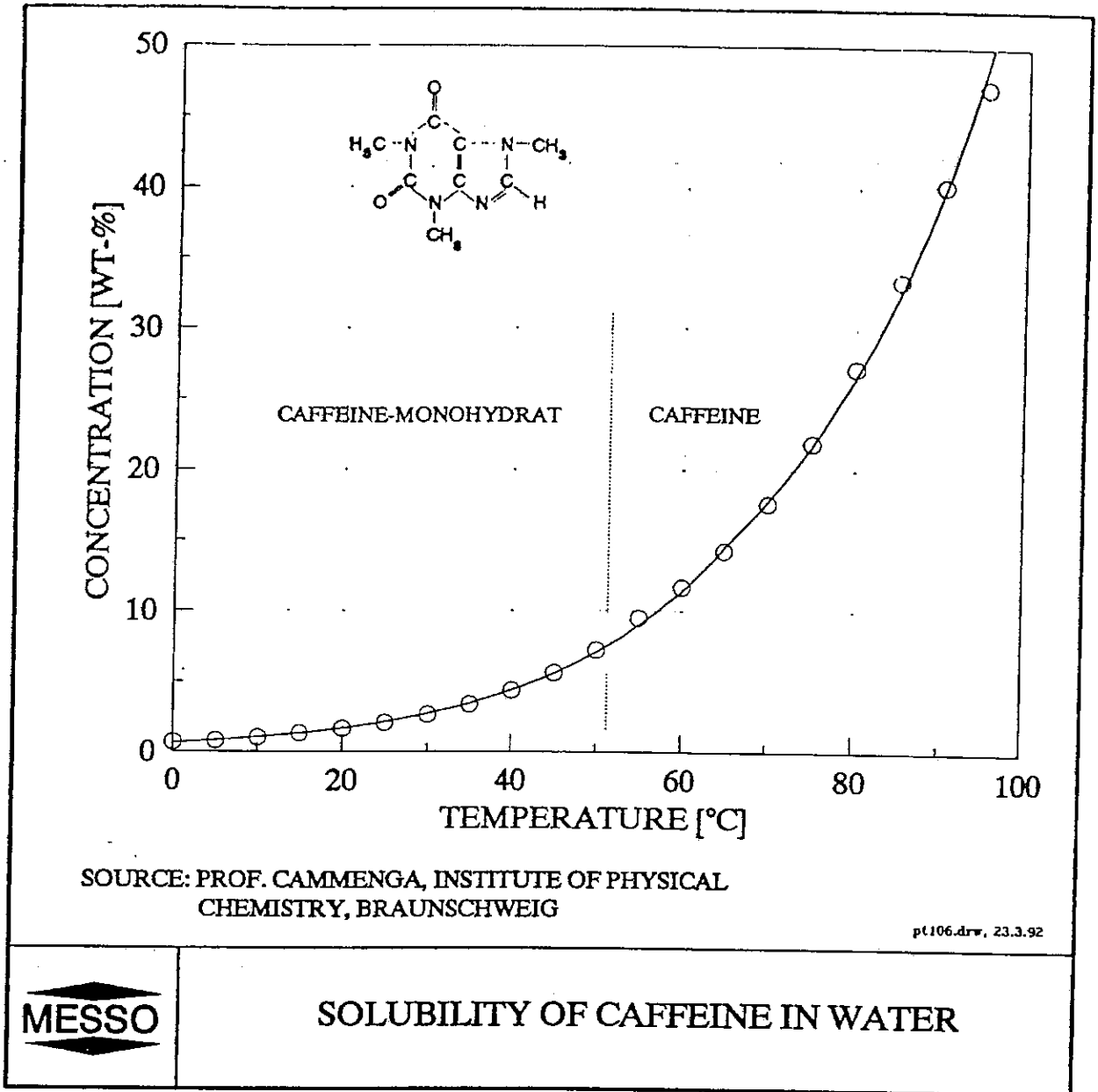
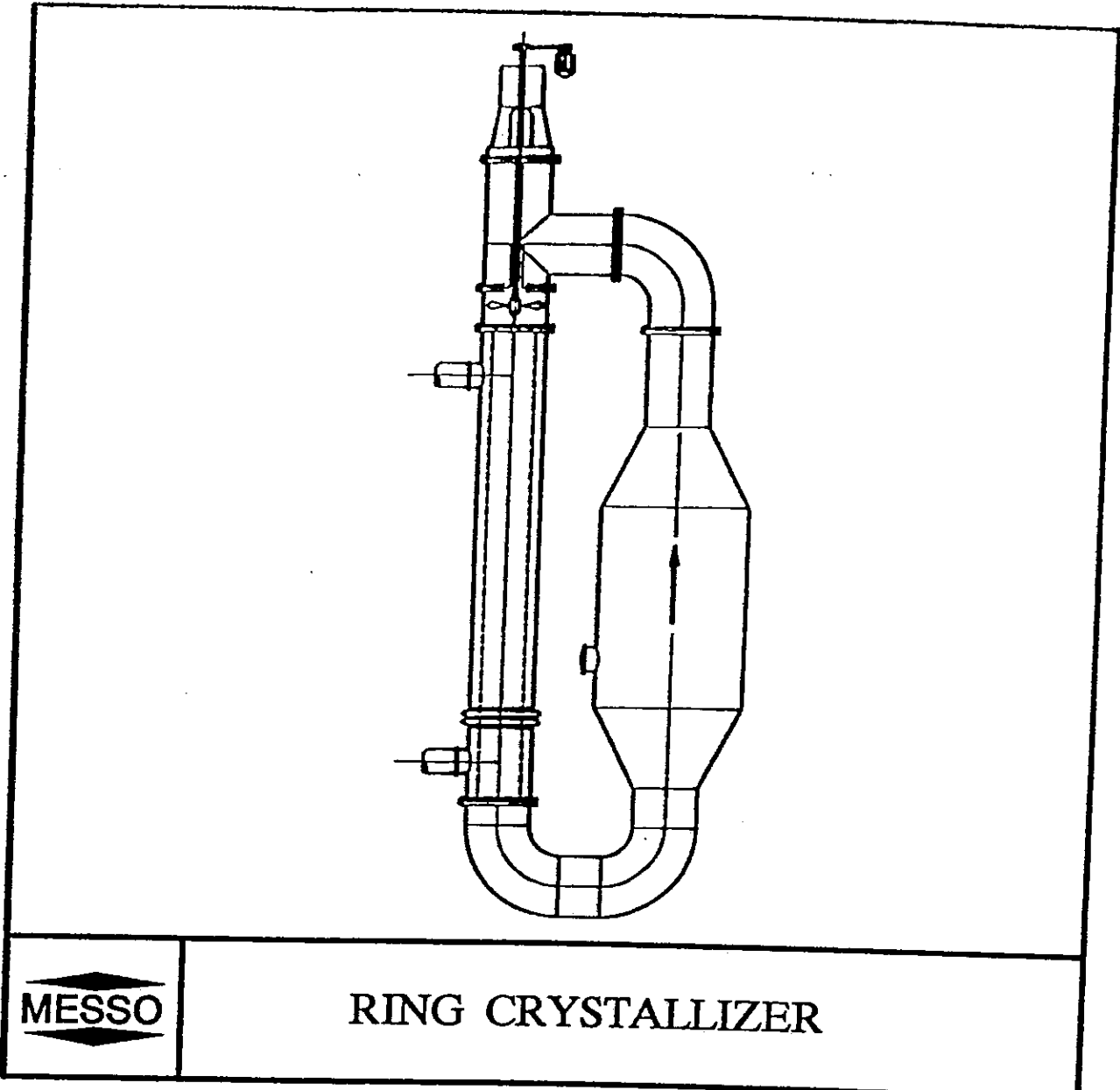


Fig. 9



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RING CRYSTALLIZER

Fig. 10