

# Recovery of Cream of Tartar from Winemaking Solid Waste by Cooling Crystallization Process

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## Abstract

Our work relates the recovery of potassium bitartrate (cream of tartar) from winemaking solid waste in Algeria. The process consists of crystallizing by cooling, separating and drying the cream of tartar. It uses water as solvent and wine tartar as raw material. This conventional method for the cream of tartar extraction has been carried out in our laboratory using batch process with a charge of 45 liters. For the various process unit operations, simple tools, not expensive and effective are used. Utilization of pipeline water filters with different cartridges (5 $\mu$ m, carbon/diatomite) has facilitated the key process operation, the hot filtration. Also, we managed to control the dissolution step, so it was monitored by continuous pH and temperature measurements in the agitated vessel, using a pH meter model DDSJ308A. And the crystallization operation was controlled using an infrared turbidity sensor developed in our laboratory.

**Keywords:** Cream of tartar; Tartaric acid; Cooling crystallization; Infrared sensor

## Introduction

Pollution from agricultural or industrial waste is considered as one of the major problems affecting the world and that may prove to be dangerous to fauna and flora. These wastes must be treated to preserve the natural balance and preserve our health. The winemaking solid waste is also known as "wine tartar"; It can be easily treated for valorization by recovering the cream of tartar and the free L (+) tartaric acid [1-7]. Thereby, reducing waste, protecting the environment and eliminating the disposal costs. In wine manufacturing, grapes are the raw material of choice. They contain tartaric acid in the potassium hydrogenotartrate form (cream of tartar). Because of their richness in this acid, they are the only source of obtaining it. This is the reason why it is recovered in the wine by-products [8-10]. The reasons which lead to its recovery are the existence of a market with reasonable prices for the calcium and potassium tartarates and the severity of the international environmental legislation for the wastes, on the other hand. Tartaric acid is the most important by-product and enjoys many foods, pharmaceutical and industrial applications. It is obtained via the decomposition of calcium tartarate by sulphuric acid. This acidification produces a sulphate precipitate of calcium (plaster) and an aqueous solution of tartaric acid. The concentration of this aqueous solution, by different technologies as electrodialysis, solvent extraction, and adsorption gives the required tartaric acid [11-15].

Cream of tartar is extracted from the wine tartar using a cooling crystallization, and water is the only solvent used. Small production does not seem suitable for continuous operation because of the problems with plugging, fouling, sedimentation of crystals in the pipes, etc.). It is better to implement in this case batch crystallization. Batch cooling crystallizers present the advantage of being simple, flexible, require less investment and, generally, involve less process development [16-20].

In our work, we have realized the optimisation of cream of tartar extraction at laboratory stage as follows:

- Volume solvent, heat temperature, mixing rate and time of extraction optimization.

- Study of the activated carbon addition or other mean of discolouration for the improvement of the quality of the final product.

Our work is based on the crystallizer behaviour study, and also to improve the performance of the method. So this laboratories work is exploited for the implementation of the process on a pilot of 45 litres. We describe different process operations for obtaining cream of tartar by batch cooling crystallization; some characteristics of equipments are discussed. Super saturation as the driving force of crystallization processes is an essential parameter, so the development of more accurate and sensitive sensors for real-time analysis of crystallization must allow significant advances in monitoring, control and optimization of crystallization processes. In a second part of our work, acquisition of temperature and pH parameters were used for control during the process. The optimization of the cooling time in the crystallizer was managed by turbidity measurements on-line was performed using an infrared sensor made in our laboratory.

## Materials and Methods

### Oenological waste

Oenological waste (Cream of tartar) was provided by an industrial plant (ONCV- hassi El- Ghala, Algeria). For the laboratory essay it has crushed, but for the pilot it was used in its raw form (Figure 1).

### Description of the process

The agitated crystallizer vessel (C) (Figure 2), technologically

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Figure 1: Cream of tartar.

simple, leads to different particle size distribution. In fact, it is the difficult stage of our process, because it requires control and monitoring.

The dissolver (D) is an agitated vessel mechanically stirred, stainless steel curved bottom, of capacity equal to 45 liters. This reactor consist of two concentric tanks, one is inside the other. The inner tank is mobile and coupled to a motor-IKA RW20 type which provides a speed range of around 300 rev/min (Figure 3).

The agitation is generated by the rotation of the inner tank which is nonsymmetrical with the outer vessel. The heating is made by two resistors of different capacities 2400 and 1000 Watts, installed between and inside the two tanks of the dissolver.

The reactor is covered by a sheet of glass, provided with holes and adaptations required to the liquid feed, the pH electrode, the temperature sensor and the condenser (F).

The dissolver is powered by the solvent (water) and tartar in its raw form, without crushing or grinding.

The crystallizer is a cylindrical steel reactor with a conical base in the form of a funnel (Figure 3), provided with a cooling coil. This later is connected to a refrigerating plant 1.6 KW. The total capacity of the crystallizer is 80 liters. It is stirred by a special stirrer, associating two types of agitators. A classic anchor and a Rushton turbine all coupled to a stirring motor with a speed reducer with 328 rev/min as range of agitation. This range of agitation was measured with a stroboscope COMPACT brand, model 461830.

The cooling crystallization process is based on a hot filtration. This operation is very sensitive to the presence of insoluble impurities causing the fooling of the filter and therefore, requiring frequent wash filter. To avoid this problem, we introduced a filter bag sized in the dissolver according to the internal walls of the tank. This bag is easy to wash and change. The dissolver is connected to the crystallizer consisting of agitated vessel with jacketed for heat exchange (cooling). The precipitate is collected and the solvent is recycled. After several crystallizations, cream of tartar is obtained in the pure form, and can be dried out and packaged.

## Results and Discussions

### Optimization of process parameters: Laboratory tests

Laboratory tests were achieved to optimize different parameters of the extraction operation: solvent volume, heating time, stirring time and stirring rate. The wine tartar, as a raw material, was provided by the different wine cellars in Western Algeria. Chemical composition

is given in Table 1. We introduced 10 grams of raw material crushed in different amounts of water (50-300 ml). After heating, boiling, hot filtrating and cooling the filtrate, the product crystallized. This product was filtered and dried at 105°C in an oven to constant weight for one hour. The results are presented in Figure 4.

According to preliminary tests we found that prolonged heating at boiling temperature caused a great loss of solvent. For this reason we carried out the extraction in the temperature range 70-90°C. As shown in Figure 5, the optimum volume is 200 ml. We studied the optimization of the heating temperature in Figure 5 in order to see the effect of low temperatures on the quality and quantity of the produced material.

The obtained results by setting the volume to 200 ml of water, confirm that the best performance may be obtained while heating to

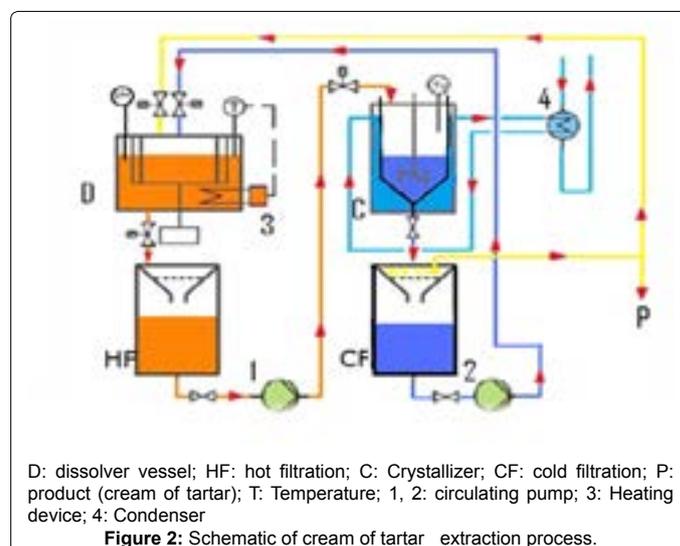


Figure 2: Schematic of cream of tartar extraction process.

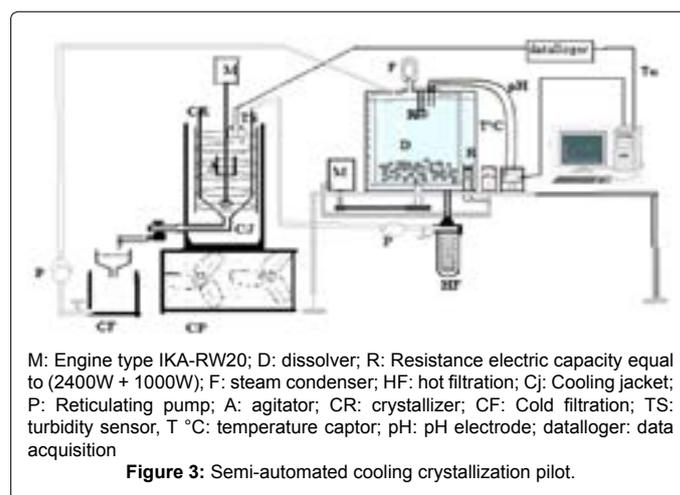


Figure 3: Semi-automated cooling crystallization pilot.

Parameters	Rate of optimization
Water (ml)	200/10g raw material
T(°C)	90-100
T (min)	10
V(rd/min)	900
Yield (%)	56 – 70

Table 1: Summary of experimental optimization results.

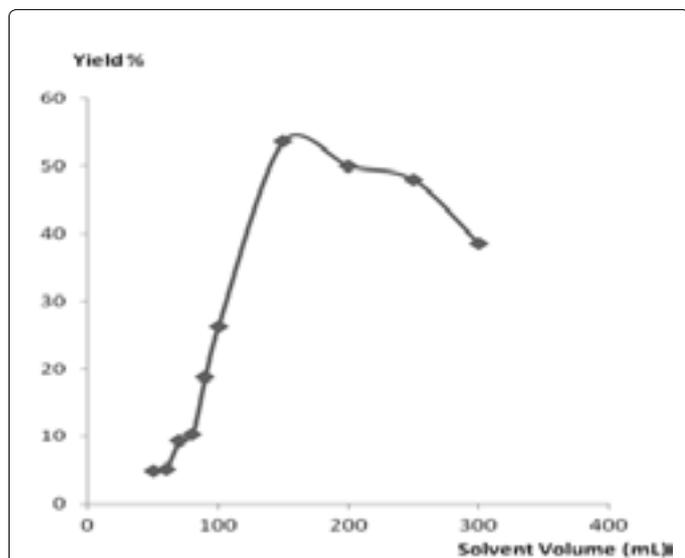


Figure 4: Change in the cream of tartar extraction yield versus solvent volume.

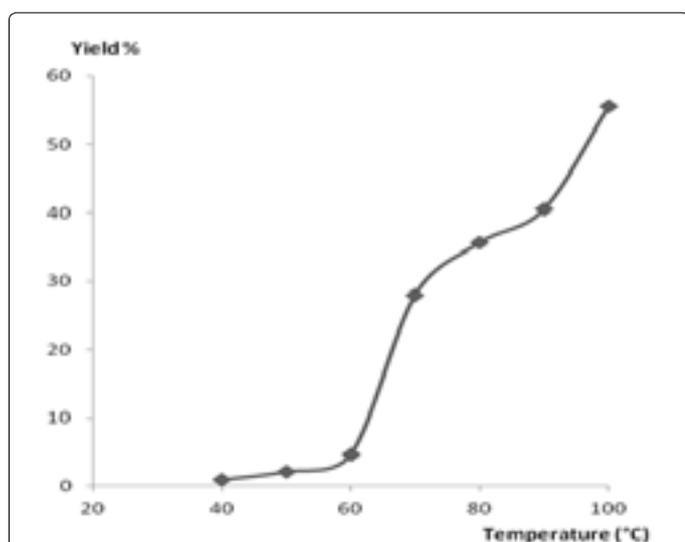


Figure 5: Change in the cream of tartar extraction yield versus heating temperature.

boiling temperature (100°C). Low temperatures extend the heating time and no improvement of the product was observed. However, we found that the yield at 90°C is approximately maximum. So, at such a temperature we avoid not only the evaporation of the solvent but energy consumption as well. Agitation is an important operation in our process. In fact it is also considered as a complex operation which is difficult to optimize and to translate the obtained results from the laboratory tests to the industrial equipment.

By maintaining the temperature at 90°C and the water volume 200 ml we performed the experiment by varying the stirring time (2 min, 5 min, 10 min) while varying the stirring rate. The rate stirring optimization results show that, a maximum yield may reached (approximately equal to 7 gr.). This can be achieved with a stirring time of 10 minutes along with agitations rates from 700 to 1000 rev/min (Figure 6).

In order to improve the quality of cream of tartar, we used the

bleaching clay (bentonite) during the dissolution stage. We used 10 to 50 mg of bentonite mixed to 10 grams of raw material. The results of the operation showed that the product quality (colour) has considerably improved from the first crystallization, but the filtration became more difficult. Besides, the insoluble residues caused the filter fooling to become too quickly.

However, the use of bentonite or other large-scale bleaching earth or powder active carbon (PAC) breaks the problem of disposal of sludge which should be avoided. The great disadvantage of bentonite and CAP was, sludge disposal and the impossibility of their regeneration. Currently, competitive to the bleaching clay is membrane filtration as reverse osmosis. In the microfiltration process diatomaceous earth is usually used as filter aid. So, our choice was ultimately focused on the use of diatomaceous earth, this choice needed to be justified and adapted to the pilot scale operation.

### Dissolver reactor temperature and flow profiles

We calculated the cream of tartar dissolution heat; this amount of heat will be useful for determining the power needed to dissipate in our dissolver reactor (D). We have prepared saturated solutions at each temperature, and we have also determined the equilibrium constant at 100°C (K).

The value and the sign of  $\Delta H$  (heat of solution) can be determined from the equation (3) below. After cream of tartar solubilisation the following equilibrium is established:



HT<sup>-</sup> : Represents the hydrogen tartarate ion

$$K = [\text{K}^+][\text{HT}^-] \quad (2)$$

$$\ln \frac{k_2}{k_1} = \frac{\Delta H_s}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) ; \quad \ln k = -\frac{\Delta H_s}{R} \left( \frac{1}{T} \right) + C \quad (3)$$

In equation (1),  $k_1$  and  $k_2$  are respectively the equilibrium constants at temperatures  $T_1$  and  $T_2$  in Kelvin, and R is the perfect gas constant. According to the graph of the equation (3), we have estimated that  $\Delta H$  is 290.79 kJ/kg.

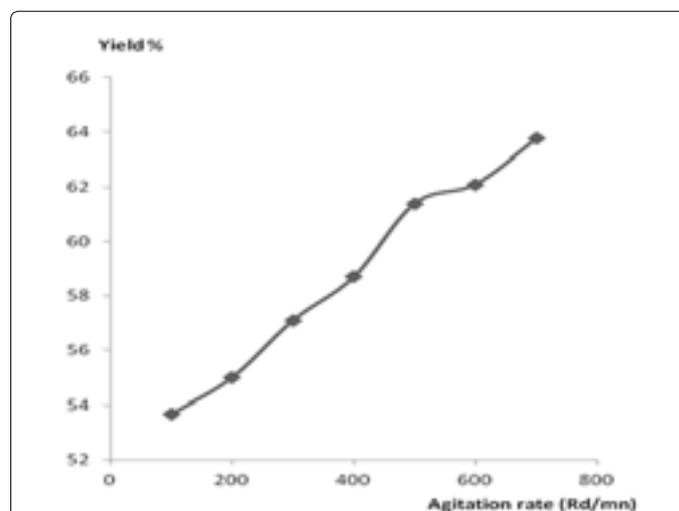


Figure 6: Change in the cream of tartar extraction yield versus rate and stirring time.

The generated flows profile by the rotation of the inside tank of the dissolver reactor (Figure 3) is presented in the Figure 7.

For mobile radial flow, the regime depends not only on the type of mixing device but on geometrical factors for the tank as baffles, eccentric shaft and size of the tank as well. In our case the flow regime is turbulent (based on the value of Reynolds number), which results in the absence of fluid motion in a direction different from that imposed by the inside tank rotation.

### Control process and monitoring

We applied a slow agitation for the dissolver and we followed the evolution of the heating temperature versus time. This monitoring was performed using the software DRAW, with a recording time of a record each minute. At the end, the results were transferred to Excel software to plot the behaviour of heating temperature and pH in the dissolver. A time of 25 mn was necessary to reach 100°C as shown in Figure 8 and 9 respectively.

The pH curve show clearly the saturation of the solution in cream of tartar at a given temperature is determined. A saturated aqueous cream of tartar solution have a pH equal to 3.4.

The pH meter model DDSJ308A automatically performs the

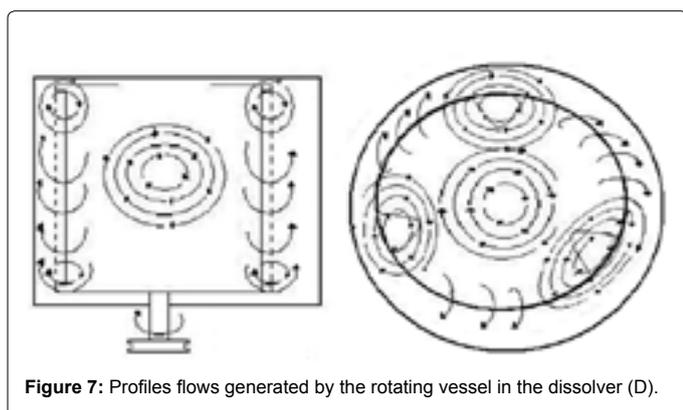


Figure 7: Profiles flows generated by the rotating vessel in the dissolver (D).

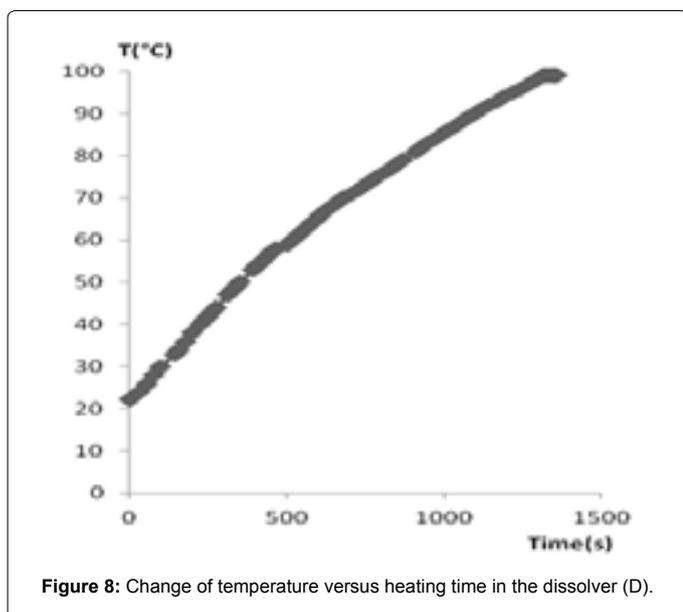


Figure 8: Change of temperature versus heating time in the dissolver (D).

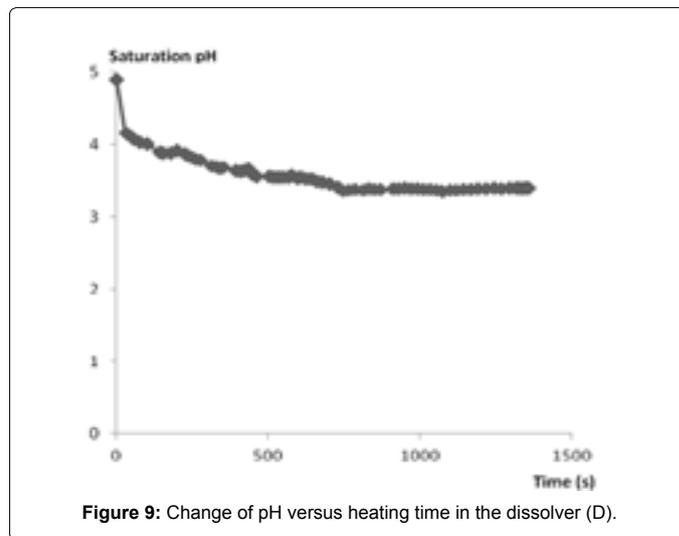


Figure 9: Change of pH versus heating time in the dissolver (D).

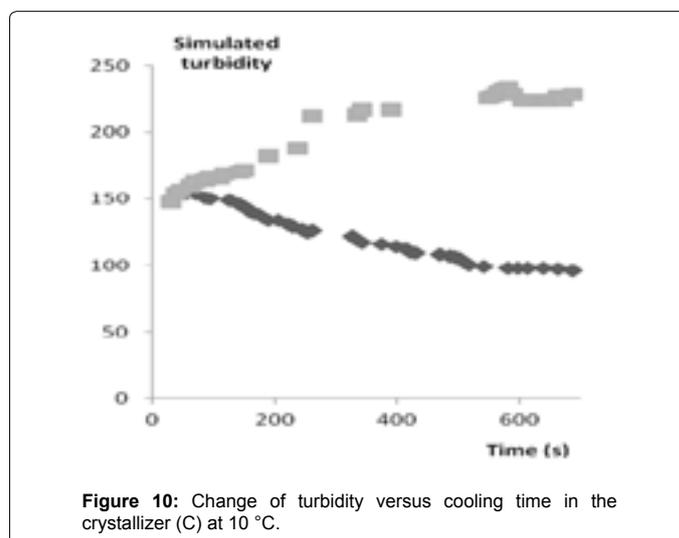


Figure 10: Change of turbidity versus cooling time in the crystallizer (C) at 10 °C.

temperature correction. This method needs a special pH electrode, and represents an excellent way to optimize the dissolution time in the dissolver. According to our test, a heating time inferior at 30 mn is necessary to achieve the saturation temperature range 95-100°C and a maximum yield of 2 kg per charge.

In the crystallization stage, it should be noted that different element of the crystallizer complicates enormously this operation by depositing a very solid crystalline layer (tartar) leading to a number of adverse consequences in the process, in particular:

- The need to clean the crystallizer;
- The lost productivity by reducing the heat transfer performance of the device if the layer covers completely the surface of exchange;
- The Difficulties in filling and clogging as deposition occurs also in the filling elements and in the pipes transfer.

To avoid these problems, the washing is done with hot water or a solution of sodium bicarbonate to minimize the time stays in crystallizer. For this purpose, turbidity in crystallizer caused by the precipitation of cream of tartar is monitored on-line by an infrared

turbidity sensor designed in our laboratory [19,20]. In Figure 10 it is shown that saturation is reached at 600 minutes at a temperature of cooling set at 10 °C (gray curve). The black curve in Figure 10 shows the effect of temperature on the measurement of turbidity using our infrared sensor; this curve represents the turbidity measurement of distilled water from 90 to 10°C. We noticed that the evolution of turbidity versus cooling time in the crystallizer can clearly indicate the end of the cooling operation.

## Conclusion

In order to use any technique on an industrial scale it is necessary to undertake laboratory and pilot trial. In our approach, we studied the behavior of a dissolver, a crystallizer and hot filtration in the laboratory. We began an audit of change of cooler temperature using an infrared camera (Ti FLUKE 10). We also realized crystallization of cream of tartar from wine waste in order to experience the batch crystallization process. Moreover, we also monitored the dissolver with the acquisition of temperature and pH on-line using a pH meter provided with RS232 output. The accuracy of off line methods for evaluating crystallization processes is strongly dependent on sampling. By using real-time analysis these types of errors can be greatly reduced. And the determination of the solubility of a solid in a specific solvent is a key step in the study of crystallization processes. So, we have used an infrared sensor of turbidity to determine the optimum cooling time made in our laboratory. Detailed study of these problems is one of our intended future works.

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