

# PREPARATION OF FEED-GRADE MONOCALCIUM PHOSPHATE BY CRYSTALLIZATION IN AQUEOUS MEDIUM: CALCULATION AND EXPERIMENTS

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Received: 3 November 2020; Accepted for publication: 9 September 2021

**Abstract.** Monocalcium phosphate is one of the most commonly used forms of inorganic feed phosphates for certain types of animals. It can be prepared by the reaction between phosphoric acid and a calcium source, the resulting slurry is then dried. In this paper, we use the graphical calculation method to quantify the formation of monocalcium phosphate in acidic solution as a guide for the experiments. The calculation and experimental results show that monocalcium phosphate can be formed in the solid phase when the reactants are added to the mother liquor at 100 °C, then this system is cooled down to 25 °C. The mother liquor plays the role of medium for the precipitation and crystallization of monocalcium phosphate. The weight ratio of the fresh phosphoric acid to the mother liquor can vary in a fairly wide range from 1:1 to 1:4. The results show that the solid yield reaches 92.4 %, the final product is a single phase with a structure similar to the one of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and contains parallelogram-like crystals with a length of about 20 - 50  $\mu\text{m}$ , a width of 20 - 30  $\mu\text{m}$ , and a thickness of a few microns. The formation of monocalcium phosphate has been confirmed by the XRD data and chemical analysis.

**Keywords:** Monocalcium phosphate, crystallization method, mother liquor, phosphoric acid, feed additives.

**Classification numbers:** 2.10.2, 2.10.3

## 1. INTRODUCTION

Many compounds in the calcium phosphate system have attracted researchers and users for a quite long time due to their interest from a technical as well as an application point of view. Monocalcium phosphate is one of the interesting food additives for animals because it provides both phosphorus and calcium, which are necessary for the growth of certain types of animals. Some studies for preparation of monocalcium phosphate under different conditions have been performed to improve the production of monocalcium phosphate [1]. The preparation by reacting phosphoric solution with calcium sources such as lime, limestone or calcium oxide, followed by directly drying the formed slurry, is widely used [2, 3]. Another approach is to use a mixture of calcium compounds to control the thermal effect of the process in order to remove water from feed stream and physically bound water composition in phosphate product [4]. In these processes, insoluble impurities, if any, from the reactants will retain in the final product.

Other routes use aqueous solutions containing organic solvents such as acetone-water, ethanol-water or methanol-water, to precipitate monocalcium phosphate even at ambient temperatures [5, 6, 7]. However, the possibility that the end products contain some solvents or impurities, may raise concerns about the use of monocalcium phosphate in feed-grade additives. Hence, the use of aqueous mother liquor as a medium for the precipitation and crystallization of monocalcium phosphate may be fruitful. After separating the solid product, the mother liquor can be recycled for further production. The mother liquor is also a liquid medium for the accumulation of impurities, if any, from the reactants, and the purification of that solution can be done separately, which offers the possibility of obtaining a cleaner product.

The graphical calculation method has been successfully applied to evaluation and quantification of various systems [8]. In this work, we used this method to calculate the crystallization of monocalcium phosphate during mother liquor recycling. The calculation results are guidelines for the experiments. Several process parameters such as temperature range, reactants to mother liquor ratio have been investigated. The composition, structure and morphology of the solid phase were also studied.

## **2. MATERIALS AND METHODS**

### **2.1. Method of calculation**

The data given by Elmore and Farr [9], meeting the requirements of industrial practice [10], are used or evaluated for the calculation. A material balance-based calculation method is chosen for the determination of reactants and products.

### **2.2. Reagents**

Calcium carbonate with  $\text{CaCO}_3$  content greater than 99.0 % (Xilong Scientific Co., Ltd.) used for experiments and chemicals for analysis are of reagent grade purity and commercially available. Phosphoric acid (85.44 %  $\text{H}_3\text{PO}_4$ , technical grade) was provided by Duc Giang Chemicals Group.

### **2.3. Synthesis procedure**

Monocalcium phosphate monohydrate can be prepared as follows: 100 g of mother liquor solution at 25 °C is heated up to about 100 °C, then a defined volume of phosphoric acid solution is added, followed by the gradual addition of the required amount of calcium carbonate. The mixture is vigorously stirred to form a homogeneous mixture. After the reaction is completed, the slurry is slowly cooled to 25 °C for several hours, and then filtered to collect the solid, which is then washed with water to remove free acid. The solid product is dried at 95 °C to constant weight. The mother liquor is recycled for further experiments.

### **2.4. Analytical methods**

The phosphorus content in the synthesized samples is determined by the magnesium-ammonia precipitation method. The calcium content in the samples is determined by titration with EDTA solution.

The crystal structure of the obtained samples is evaluated by X-ray diffraction (XRD) using a D8 Advance Bruker diffractometer with Cu anode,  $\lambda(\text{CuK}\alpha) = 1.54056 \text{ \AA}$ , recorded at room temperature. The morphology of the samples is measured by scanning electron microscopy on a NANOSEM450 equipment.

### 3. RESULTS AND DISCUSSION

#### 3.1. Calculation for the preparation

The data given by Elmore and Farr [9] showed that monocalcium phosphate can be prepared by crystallization in a solution of phosphoric acid, and that the area or zone of crystallization depends on the temperature and composition of the mixture. The crystallization of monocalcium phosphate can be performed at 25 °C; however, the temperature of the reaction mixture can be increased due to the heat generated during neutralization of phosphoric acid and the calcium source, and crystallization processes. The reaction temperature may vary due to process design and operation. Supposing that the reaction temperature is 100 °C, some water can be evaporated, and monocalcium phosphate is formed. When the slurry is cooled, e.g. to 25 °C, monocalcium phosphate is crystallized and can be separated from the slurry. The obtained mother liquor with a composition of intercepts of liquidus at 25 °C and the extension of monocalcium phosphate hydrate point to the solution at 100 °C, is recycled by the addition of phosphoric acid and a calcium source. Therefore, a lot of data will be available provided that precipitation and crystallization are in the zone of monocalcium phosphate. For simplicity, we present a calculation for a solution at 100 °C with the smallest amount of residual phosphoric acid in solution (as point Q, in the supporting information, SI) with an evaluated composition of CaO, P<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O of 5.5518, 40.1582, and 54.29 % bw, and the intercept (L) at 25 °C with a composition of 2.8247, 37.4243 and 59.7510 % bw, respectively.

Supposing that 100 grams of mother liquor at 100 °C is cooled down to 25 °C, the contents of the solution will be changed and the material balance of each composition will be:

$$100 \text{ g (sol at Q)} = x_1 \text{ g (Ca(H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O)} + y_1 \text{ g (solution at L)} \quad (1)$$

$$\text{For CaO balance: } 5.5518 = 0.2225x_1 + 0.028247y_1 \quad (2)$$

$$\text{For P}_2\text{O}_5 \text{ balance: } 40.1582 = 0.5631x_1 + 37.4243y_1 \quad (3)$$

Solution of equations 2 and 3 gives  $x_1 = 14.042 \text{ g}$  and  $y_1 = 85.958 \text{ g}$

After the solid phase is separated, the mother liquor is heated up, then H<sub>3</sub>PO<sub>4</sub> (85.44%) and CaO (or other calcium sources) are added to give Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and 100 g solution at Q after the reaction finished. The material balance can be represented as:

$$x_2 \text{ g CaO} + y_2 \text{ g (H}_3\text{PO}_4 \text{ 85\%)} + 85.958 \text{ g solution at L} = z_2 \text{ g (Ca(H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O)} + 100 \text{ g solution at Q} + a_2 \text{ g H}_2\text{O} \quad (4)$$

By combining equations (1) and (4), we obtained

$$x_2 \text{ g CaO} + y_2 \text{ g (H}_3\text{PO}_4 \text{ 85.44\%)} = z_2 \text{ g (Ca(H}_2\text{PO}_4)_2\cdot\text{H}_2\text{O)} + a_2 \text{ g H}_2\text{O} \quad (5)$$

This equation is similar to the reaction of CaO and H<sub>3</sub>PO<sub>4</sub>. It means that the mother liquor serves as the medium for the precipitation and crystallization of monocalcium phosphate monohydrate while the relative ratio of the fresh reactants to the mother liquor can vary in certain ranges.

### 3.2. Experiments based on the calculation data

Because the preparation reaction does not depend on the relative amounts of the fresh reactants and the mother liquor, experiments were performed with 100 grams of mother liquor at 25 °C and 100, 50, and 25 grams of phosphoric acid solution at a concentration of 85.44 %. The amount of calcium carbonate as the CaO source is calculated from the amount of phosphoric acid used for the experiments. The experimental results are summarized in Table 1.

Table 1. Effect of weight ratio between phosphoric acid solution and mother liquor on solid product formation.

Designation	Weight of phosphoric acid solution, g	Weight of calcium carbonate, g	Weight of mother liquor, at 25 °C, g	Weight ratio between phosphoric acid solution and mother liquor	Weight of product, g	Yield %
C100	100	44	100	100/100	99.87	90.0
C50	50	22	100	50/100	51.31	92.4
C50(2)	50	22	100	50/100	51.14	92.1
C25	25	11	100	25/100	24.50	88.5

Table 1 shows that, in all experimental cases, the yield of solid phase is quite high, reaching approximately 90 %. In the experiment denoted C50, at a weight ratio of 50 g of phosphoric acid solution to 100 g of mother liquor, the solid product is obtained at an yield of 92.4 %, slightly higher than that in the remaining experiments. It should be noted that in the experiments, after filtration, the solid phase is washed with water so that some monocalcium phosphate is dissolved into the filtrate. The amount of dissolved monocalcium phosphate depends on the amount of water used for filtration. The filtrate recovery will be covered in another study and once the filtrate is recovered, the yield will be improved.

To examine the ability of recycling crystallized solution (C50(2)), the mother liquor from the C50 experiment is recycled under similar conditions to those of C50, the results show that the solid phase is equivalent to that of C50. The chemical composition of CaO, P<sub>2</sub>O<sub>5</sub> and H<sub>2</sub>O in the mother liquor of C50 is 2.73, 37.09, and 60.18 % respectively, very close to the previous cycle with values of 2.82, 37.42 and 59.75 % at 25 °C. The calculation and experiments show that the preparation of monocalcium phosphate can be done with the recycling of mother liquor.

### 3.3. Chemical composition and phase of the synthesized product

The chemical analysis of the solid phase of the first (C50) and the second (C50(2)) cycles are given in Table 2.

Table 2 shows that the chemical compositions of these samples are similar. The calcium and phosphorus contents in sample C50 are 15.87 and 24.26 %; in sample C50(2) are 15.99 and 24.15 %, respectively, very close to the values of 15.89 and 24.58 % of calcium phosphate monohydrate, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O.

Table 2. Chemical composition of solid products.

Sample designation	P content, % bw	Ca content, % bw
C50	24.26	15.87
C50(2)	24.15	15.99

The crystal structure of the samples in Table 1 is determined by powder X-ray diffraction. The measurement results on these samples are shown in Figure 1.

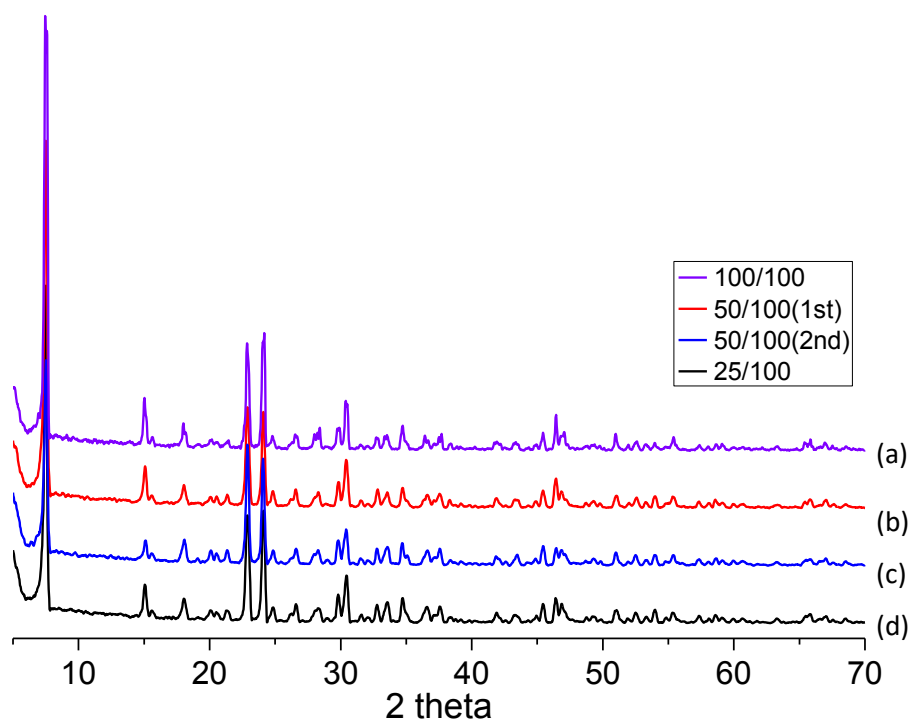


Figure 1. XRD powder patterns of the final products of C100 (a); C50 (b); C50(2) (c), and C25 (d).

Figure 1 shows that the XRD powder patterns of these samples are similar, and they are consistent with the structure of  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  in our previous work [3]. It means that all synthesized products are single phase with the same  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  structure as expected.

### 3.4. The morphology the synthesized products

The morphology of the synthesized products is evaluated by scanning electron microscopy and the results are given in Figure 2.

Figure 2 shows that all synthesized products contain parallelogram-like particles, most of which are quite large, while others are somewhat smaller. The average crystal size is about 20 - 50  $\mu\text{m}$  in length, 20 - 30  $\mu\text{m}$  in width, and a few microns in thickness. The morphology of the crystals in these experiments is similar to that of the crystals synthesized in the aqueous medium in our previous work, in which the crystal size is somewhat more regular [3].

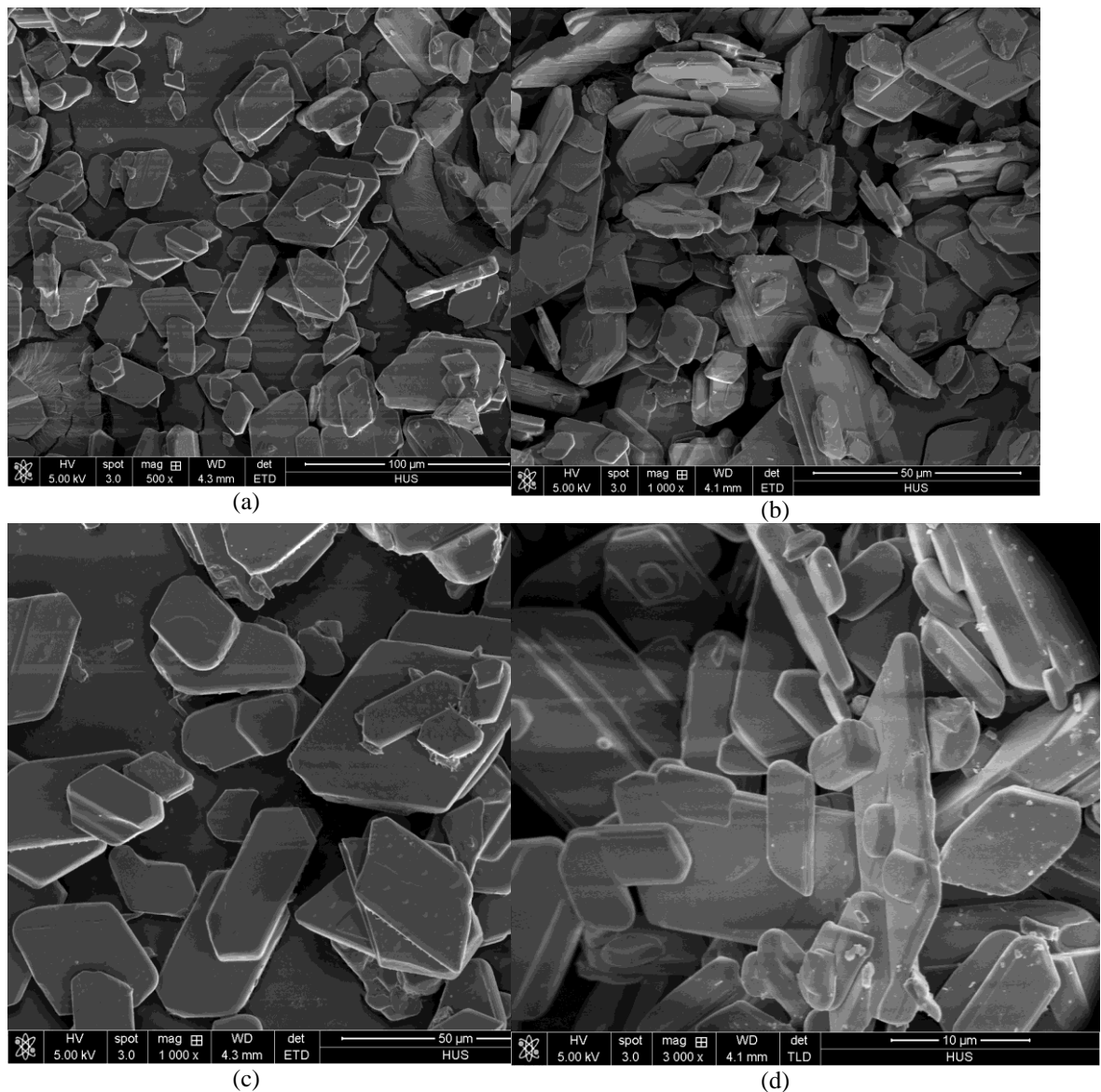


Figure 2. SEM images of samples C100 (a), C50 (b), C50(2) (c) and C25 (d) of the synthesized products.

#### 4. CONCLUSIONS

The graphical calculation method for calcium phosphate aqueous system has been successfully implemented and the results of the experiments confirmed the calculation results. Monocalcium phosphate monohydrate can be prepared from phosphoric acid and calcium carbonate in a recyclable mother liquor with high yield and a single phase. The reaction is carried out at 100 °C, and after the slurry is cooled down (e.g. to 25 °C), the product is formed through precipitation and crystallization. After the solid phase is separated, the mother liquor can be reused for the next cycle. The weight ratio of fresh phosphoric acid to the mother liquor can

vary over a fairly wide range from 1:1 to 1:4. The results show that the yield of the solid product is achieved at 92.4 %, the final product is a single phase with the same structure as  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and contains parallelogram-like crystals, with about 20 - 50  $\mu\text{m}$  in length, 20 - 30  $\mu\text{m}$  in width, and a few microns in thickness. The use of a liquid medium for preparation and crystallization makes the production process easy to control in practice because it acts as a buffer against changes in phosphoric acid or calcium content in the feed stream. During the crystallization of monocalcium phosphate monohydrate, when the slurry is cooled down, the content of dicalcium phosphate, if previously formed, will decrease as it depends on the solubility at negative temperatures. As a result, the final product will be of higher purity, suitable for feed additive applications. The less than expected solid phase yield is due to the washing of the solid with some water, which has not been calculated in this work.

Research to improve product yield and optimize precipitation and crystallization on other mother liquor preparations, or to use other calcium sources such as calcium oxide and dicalcium phosphate is still in progress.

**Acknowledgements.** The authors would like to thank Mr. Dao Huu Huyen, CEO; and Mr. Dao Huu Duy Anh, General President - DUC GIANG CHEMICALS GROUP for the research support and chemical supply.

**CRedit authorship contribution statement.** Nguyen Quang Bac and Ta Hong Duc carried out the main experimental work, collected and analyzed experimental data, designed and discussed the study and wrote the manuscript together.

**Declaration of competing interest.** The authors have declared no conflict of interest

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