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INVESTIGATION OF SOME FACTORS INFLUENCING THE FORMATION OF MONOCALCIUM PHOSPHATE IN AQUEOUS MEDIUM

Ta Hong Duc, Nguyen Quang Bac*

School of Chemical Engineering, Hanoi University of Science and Technology, No. 1 Dai Co Viet St., Ha Noi

*Email: *bac.nguyenquang@hust.edu.vn*

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Abstract. Some factors that influence the formation of monocalcium phosphate in aqueous solution have been investigated in detail. The results show that reaction temperature, initial concentration of phosphoric acid and reaction duration determine the content of monocalcium phosphate in the processing mixture. The information in this report will be useful, and provide the basis for the design of synthesis reactor in monocalcium phosphate production.

Keywords: Monocalcium phosphate, dicalcium phosphate, reaction rate, phosphoric acid, interaction duration.

Classification numbers: 2.10.1, 2.10.2, 2.10.3.

1. INTRODUCTION

Feed phosphates are of great importance among animal feed additives produced for intensification of livestock farming, which enables compensation of phosphorus and calcium deficiency in the feeds [1]. Feed phosphates are mainly monocalcium or dicalcium phosphates which are typical examples in the system of $CaO–P_2O_5–H_2O$.

Various methods to prepare or optimize the production of monocalcium phosphate have been used or tried [2, 3]. However, the solution-based methods such as the crystallization in aqueous solutions or precipitation from aqueous solutions containing organic solvents are still widely applied because it facilitates the formation of polycrystalline homogeneous particles with improved properties [3–5]. Previously, we reported the synthesis and characterization of monocalcium phosphate in aqueous medium [6]; however, certain parameters that influence the formation of monocalcium phosphate have not been investigated. This work will study these parameters in detail to give useful information to design the production of monocalcium phosphate as well as the operation afterward.

2. MATERIALS AND METHODS

2.1. Reagents

All chemicals, except phosphoric acid, are of reagent grade and commercially available. Phosphoric acid was supplied by Duc Giang chemicals and detergent powder joint stock company. All chemicals were used as received without any further purification.

2.2. Synthesis procedure

The typical procedure for the synthesis of monocalcium phosphate monohydrate is as follows: 1.0 g of 85.44 % H_3PO_4 was diluted with 0.7 mL of water, then the formed solution was heated to designated temperature in water bath. Calcium carbonate (0.44 g) was then added, and the slurry was stirred continuously to form homogeneous mixture. The content of monocalcium phosphate, dicalcium phosphate, and free acid, if any, in the sample is evaluated for different reaction time.

2.3. Product evaluation methods

The total fraction of monocalcium phosphate and free phosphoric acid (calculated based on the content of P_2O_5) in the mixture with dicalcium phosphate is determined by titrating with standard NaOH solution using phenolphthalein as the indicator.

The fraction of free phosphoric acid in the mixture is determined by the Yamazoe's method [7], which can be summarized as follows: The free phosphoric acid in the mixture is first extracted with the acetone-ether (1:1) mixture in several stages, then the obtained solution is carefully evaporated to free organic solvents. A few mL of water is then added and the sample is titrated with standard NaOH solution using dimethyl yellow as the indicator.

The fraction of dicalcium phosphate is evaluated as the difference between the total content of input phosphorus and those in the monocalcium phosphate and free phosphoric acid in the mixture.

The presence of impurities in the dry product after drying to constant weight, is determined with the inductively coupled plasma-mass spectrometry (Elan DRCe, Perkin Elmer).

3. RESULTS AND DISCUSSION

After adding calcium carbonate into phosphoric acid solution, the slurry formed composes of various components such as monocalcium phosphate monohydrate, or anhydrous form, dicalcium phosphate and free phosphoric acid or even calcium phosphate, and water. For simplicity, we suppose that the mixture contains monocalcium phosphate, dicalcium phosphate, free phosphoric acid and water only. Content of these components depends on the synthesis conditions such as reaction temperature, reaction time, the content of water in the mixture or initial concentration of phosphoric acid solution, the evaporation of water from reaction mixture. Hence, the investigation of the fraction of these components in the reaction mixture will give information on their interaction or transformation as well as the guide for the evaluation of product quality.

3.1. The effect of reaction time on the fraction of components

The reaction between phosphoric acid and calcium carbonate in aqueous medium can be considered as the partial neutralization of a multi-acid and a solid base. The interaction is not only the acid-base neutralizing but also the transportation of the reactant and reaction products.

The neutralizing of the reactants can be performed at room temperature, or even lower. However, the reaction mixture forms a slurry and it takes long time to evaporate water from the mixture. In addition, the reaction is exothermic and the reaction temperature will go up when the process proceeds, and the investigation of the parameters at higher temperature will be meaningful, which has been chosen in the research.

The influence of reaction time on the fraction of components in the mixture at elevated temperature has been studied. The phosphoric acid is diluted with water to form solution with a concentration of about 50 % H_3PO_4, and the formed solution is heated up to 50 °C in water bath, then, calcium carbonate is added and the slurry was stirred continuously to form homogeneous mixture. The results of analysis for each species in the reaction mixture (expressed in the fraction of P_2O_5 in each ingredient) show that the species fraction changes gradually with the interaction time as shown in Figure 1.

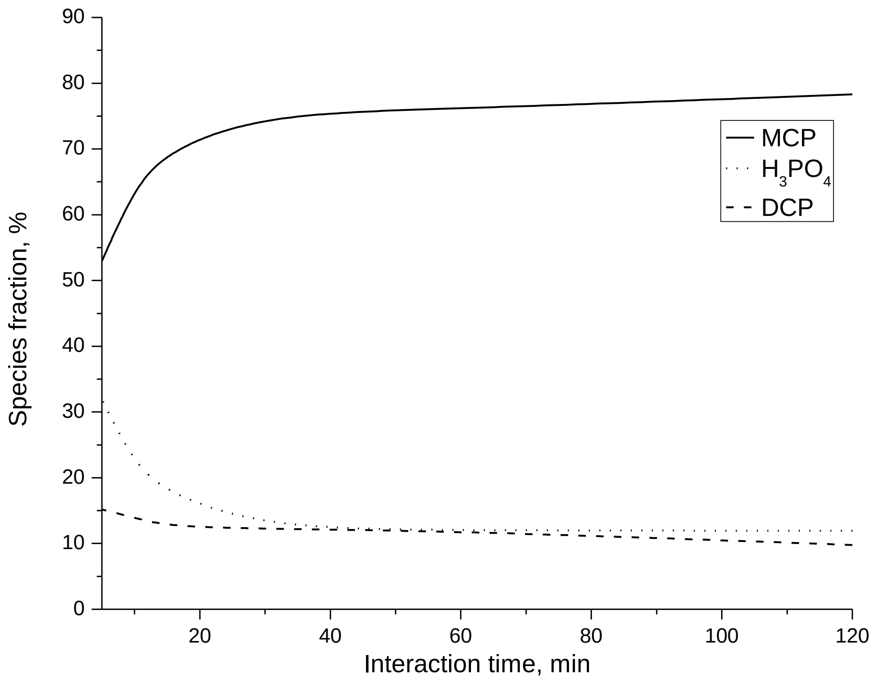

Figure 1. The influence of interaction duration on species fractions of monocalcium phosphate (MCP, solid curve), free phosphoric acid (H_3PO_4, dotted curve), and dicalcium phosphate (DCP, dashed curve) in the mixture at 50 °C.

Figure 1 shows that the fraction of monocalcium phosphate increases when increasing interaction time. The conversion of phosphoric acid to monocalcium phosphate of around 78 % is reached after 120 min. This result is comparable to the one from other work [8]. For about initial 30 minutes, the content of monocalcium phosphate increases rather fast, and becomes slower when the mixture is held for longer time. In addition, the fraction of free phosphoric acid decreases in a similar manner. It is noted that the mixture may also contain small fraction of dicalcium phosphate. The existence of dicalcium phosphate and free phosphoric acid is due to the interaction between components such as the disproportion of the incongruent monocalcium phosphate in solution or in dilute solution that favors the formation of dicalcium phosphate.

When water in the reaction mixture is evaporated, the concentration of free phosphoric acid becomes higher and the fraction of dicalcium phosphate will react with the free acid to become monocalcium phosphate and the crystallization zone may change into the one of monocalcium phosphate, that help to reduce content of dicalcium phosphate and free phosphoric acid in the reaction mixture [9]. In these experiments, the reaction temperature is maintained at 50 °C, so the water may evaporate slowly, that explains it takes rather long time to reduce the fraction of dicalcium phosphate in the product. For 120 minutes, the fractions of dicalcium phosphate, and free phosphoric acid in the reaction mixture are 9.76, and 11.93 %, respectively. In order to obtain monocalcium phosphate, all the water brought in the reaction mixture must be removed, therefore the drying process may also play an important role for the formation of the designated product.

3.2. The effect of reaction temperature on the fraction of components

As noted in the previous section, the reaction between calcium carbonate and phosphoric acid in aqueous medium is exothermic and the temperature of the reaction mixture may increase up to some levels [1]. In addition, the temperature also affects the reaction rate [10], or the transfer or diffusion of the component in the reaction mixture. The reaction temperature also affects the rate of water evaporation from the mixture if the reaction is performed in open vessels.

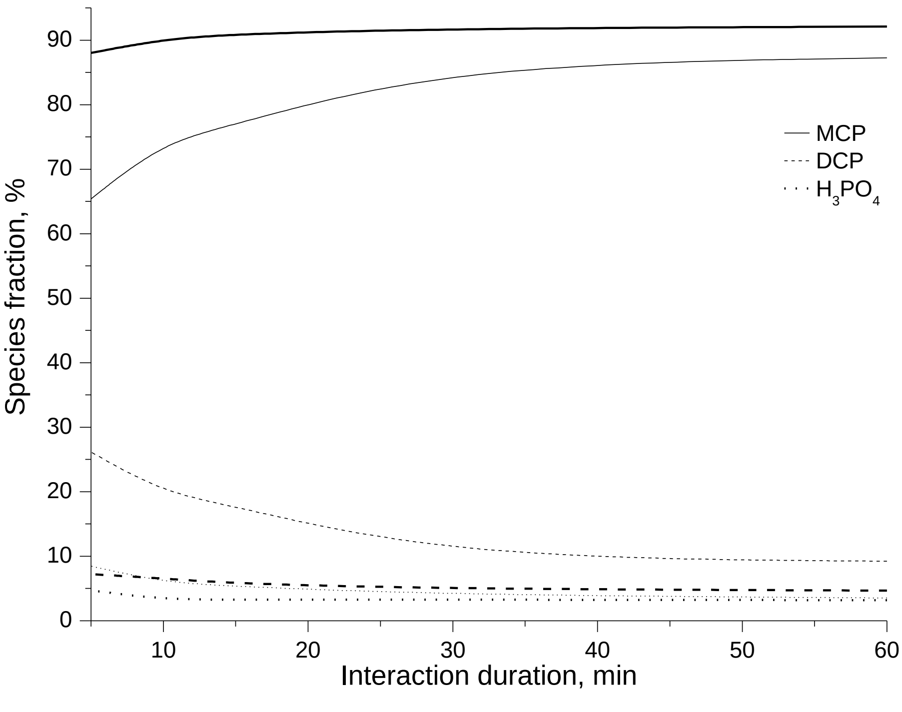

Figure 2. The influence of interaction time on species fractions of monocalcium phosphate (MCP, solid curve), free phosphoric acid (H_3PO_4, dotted curve)), and dicalcium phosphate (DCP, dashed curve) in the mixture, at 70 °C (thin curves) and 90 °C (thick curves).

The influence of the reaction temperature on species fraction in the reaction mixture has been investigated at 70 and 90 °C, with a variation of interaction time from 5 to 60 minutes. The results are shown in Figure 2.

From Figure 2, it is clear that at higher temperature, monocalcium phosphate can be formed at higher rate due to the reaction rate as well as the rate of removing water in the mixture. For the experiments at 70 °C, and 90 °C for 10 min of interaction, the results show that the fraction of monocalcium phosphate is about 74 and 90 %, respectively. The short reaction time is due to the nature of the acid-base interaction in neutralization step. When the mixture is held for 60 min, the fraction of monocalcium phosphate is about 87 and 92 %, respectively. Hence, the rate of the water evaporation may control the formation and the fraction of monocalcium phosphate in the mixture. At lower temperature, the rate of reaction and the evaporation of water will become slower and the preparation of monocalcium phosphate may require longer time. At higher temperature, the reaction rate and the interaction will become faster and it takes shorter time for the preparation. However, if the temperature is too high, water will be evaporated too fast and the mixture will become a hard solid in very short time, causing difficulty for the reactants to come to each other. The observation here also agrees well with the other results reporting that the optimum temperature for the preparation of monocalcium phosphate is about 85 °C [8].

3.3. The influence of initial concentration of phosphoric acid

As mentioned earlier, the evaporation of water from the reaction mixture is important for the formation of monocalcium phosphate and the interaction of phosphate species in the reaction mixture. In other words, the initial concentration of phosphoric acid will play an important role in the preparation and the fraction of monocalcium phosphate.

The amount of water in the system also affects the temperature and the homogeneity of the reaction mixture, and hence, the product quality. The influence of initial phosphoric acid concentration on the fraction of free phosphoric acid in the reaction mixture at 50 and 90 °C for 10 minutes is shown in Figure 3.

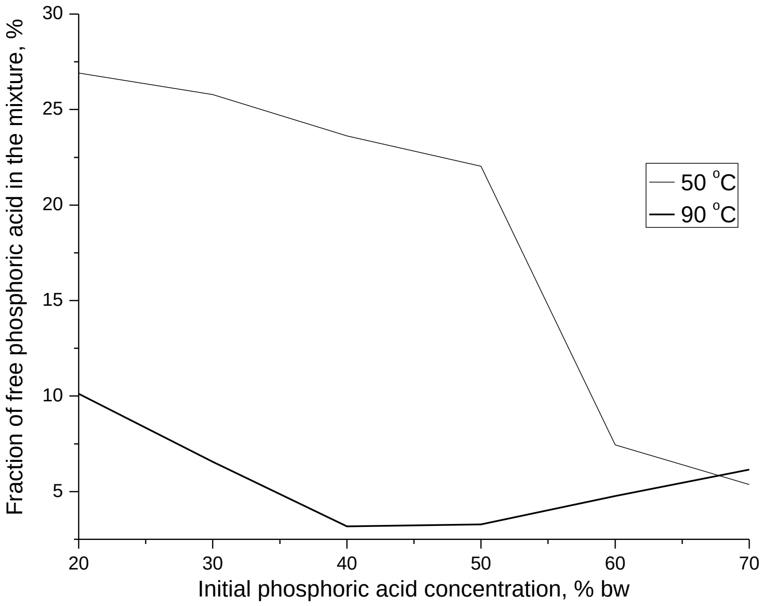

Figure 3. The influence of initial phosphoric acid concentration on the fraction of free phosphoric acid in reaction mixture at 50 (thin lines) and 90 °C (thick lines) for 10 minutes of the interaction.

Figure 3 shows that the initial concentration of phosphoric acid plays an important role on its fraction in the reaction mixture. When the concentration is low, 20 or 30 % H_3PO_4, a large amount of water will be brought into the reaction mixture that will favors the disproportionation of monocalcium phosphate to free phosphoric acid and dicalcium phosphate, especially at low reaction temperature. In addition, after the neutralization completed, all water from phosphoric acid stream (and from calcium stream) must be evaporated in order to prepare solid form of monocalcium phosphate, hence the drying step must be intensified, that may consume some more energy for the operation.

In case of high phosphoric acid concentration, 60 or 70 % H_3PO_4, at low temperature, the fraction of free phosphoric acid is low due to the small fraction of liquid phase and high concentration of phosphoric acid in the reaction mixture and crystallization zone will be on that of monocalcium phosphate. Thus, the fraction of monocalcium phosphate in the reaction mixture will be increased. However, when the reaction temperature is high, it may be not enough liquid phase for the formation of homogeneous reaction mixture because the water will evaporate too fast, and the phosphoric acid may not come into contact with the calcium source. That explains the increase of free phosphoric acid fraction in the mixture when the concentration becomes higher than 50 %. Hence, the initial concentration from 40 to 50 % will be suitable for the production process. This observation is very important for the production in large scale, because we can use the acid from purification plant instead of thermal phosphoric acid of high price.

In addition, the trace element analysis results of a typical product sample showed that the content of As is smaller than 26 ppb; Cd < 13 ppb, Pb < 0.21 ppm and F is 0.147 %. These values indicate that the obtained product meets the requirements for the animal-food additives.

4. CONCLUSIONS

The influence of some important parameters such as reaction temperature, initial phosphoric acid concentration, and the dwelling time on the formation of monocalcium phosphate has been investigated. In addition, the content of dicalcium phosphate and free phosphoric acid in the reaction mixture is also evaluated at various conditions, which gives some information of the species change after reactants added. The neutralizing period may be rather short due to the nature of the acid-base interaction, whereas the water evaporation time in many circumstances will determine the fraction of each component in the mixture as well as the quality of the final product. The parameters studied here may give some guide for the design of monocalcium phosphate production.

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