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SUSTAINABLE TECHNOLOGY OF POTASSIUM DIHYDROGEN PHOSPHATE PRODUCTION AND LIQUID WASTE RECOVERY

Summary of Doctoral Dissertation
Technological Sciences, Chemical Engineering (05T)

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ATLIEKŲ PANAUDOJIMO TECHNOLOGIJA

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1. INTRODUCTION

Relevance of the work. In the context of the systematic growth of the worldwide population without the increase of the total area of arable land, the sufficient amount and quality of food products may only be ensured by employing all the available strategies contributing to the efficiency of agriculture. In order to achieve the maximum potential of fertility of various crops, fertilizers are being used and their manufacturing technologies are being systematically improved, novel fertilizers are being devised, and new methods of obtaining fertilizers in more efficient ways are being sought after. The focus of scholarly research has been directed towards the use of renewable resources, i.e. the use of various types of biomass in agriculture; however, biomass in itself fails to ensure the full range of the nutrients to the crops as specific elements which are vital to plants may be absent. Biomass may also fail to ensure the right ratios of nutrients needed to specific species of plants, periods of their growth, climatic conditions, etc.

One of the ways of boosting the impact of fertilizers is the production of concentrated fertilizers featuring the use of the cheapest available raw materials and the simplest method of manufacturing. A highly concentrated fertilizer is potassium phosphates (potassium hydrogen phosphate and potassium dihydrogen phosphate) which, unfortunately, is usually prohibitively expensive due to excessive manufacturing costs. As a result of high prices, the commonly used potassium dihydrogen phosphate is usually restricted to highly chlorine-sensitive plants, i.e. flowers and vegetables grown in greenhouses.

The production of potassium dihydrogen phosphate commonly involves highly expensive raw materials which are hard to obtain, for example, phosphoric acid is neutralized with potassium hydroxide or potassium carbonate. The replacement of these costly substances with cheaper substituents would consequently make the final product cheaper thus increasing the viability of its use. The fertilizer industry is familiar with the technology (which actually is in widespread use) of the replacement reaction (technical conversion) of potassium chloride and ammonium nitrate yielding potassium nitrate which is also a highly valuable fertilizer. The production of potassium nitrate in such a way does not require consumption of expensive raw materials (potassium hydroxide and nitric acid); hence, the product becomes cheaper and thus more appealing to its consumers. It is likely that under specific conditions in the process of conversion of potassium chloride and ammonium dihydrogen phosphate it would be possible to obtain potassium dihydrogen phosphate which might serve as concentrated chlorine-free phosphorus- and potassium-based fertilizer. In the course of the replacement reaction, the product, i.e. the liquid phase, could be separated by filtering and further used for the production of a liquid complex fertilizer. Hence
the method of conversion would enable the production of a granular chlorine-free PK fertilizer and a liquid NPK fertilizer suitable for fertilizing fields.

There is no data concerning the production of potassium dihydrogen phosphate from potassium chloride and ammonium dihydrogen phosphate via conversion. This field of research is of major importance as it would deliver not only a simple and cheap method of production of a granular concentrated chlorine-free fertilizer containing phosphorus and potassium but would also reduce the amount of industrial waste because the liquid phase would be employed for producing a liquid fertilizer. As the outlined raw materials could potentially deliver a cheaper product, it could be used not only for greenhouse growing but for a wider array of plants.

The aim of the work is to determine the condition of potassium dihydrogen phosphate received by interaction in aqueous solutions of potassium chloride and ammonium dihydrogen phosphate and to suggest a technology of production of waste-free bulk phosphorus-potassium fertilizer and a liquid ammonia-phosphorus-potassium fertilizer.

In order to achieve the aim, the following objectives had to be dealt with:

1. To determine the products in aqueous solutions of potassium chloride and ammonium dihydrogen phosphate and to establish the optimum conditions for obtaining potassium dihydrogen phosphate via conversion.

2. To investigate and assess the influence of different granulation methods to the chemical and physical properties of the granulated potassium dihydrogen phosphate and to choose the most appropriate method of granulation as well as the best parameters of granulation process.

3. To examine the interaction of the liquid phase produced in the course of conversion with urea and ammonium nitrate, to derive the composition of the liquid NPK fertilizer and to assess the chemical and physical properties of the derived product as well as its agrochemical efficiency.

4. To produce a conceptual technological scheme for the production of granulated potassium dihydrogen phosphate and liquid complex ammonia-phosphorus-potassium fertilizers from potassium chloride and ammonium dihydrogen phosphate.

Scientific novelty

1. The equilibrium parameters of potassium chloride and ammonium dihydrogen phosphate in aqueous solutions has been researched and the optimal conditions for obtaining potassium dihydrogen phosphate via conversion have been found
2. The phase equilibrium diagrams from the remainder liquid phase after potassium chloride and ammonium dihydrogen phosphate interaction (mother liquid) have been established, and the influence of the urea and ammonium nitrate additives has been assessed.

Practical value
1. Assessment of the interaction of the mother liquid with urea and ammonium nitrate liquid 4–5–15 NPK fertilizer has been performed.
2. A conceptual technological scheme for the production of a granulated complex PK fertilizer and for the manufacturing of a liquid NPK fertilizer has been suggested.

Approbation and publication of the thesis
Two articles have been published on the topic of the present thesis in Clarivate Analytics Web of Science database journals with a citation index. 5 publications have been presented in conference materials. Together with co-authors, an application for a patent of the Republic of Lithuania has been submitted.

The extent of the thesis
The thesis consists of an introduction, analysis of data presented in scholarly literature, the methodological part, research results and their generalization, conclusions, a list of 123 sources used as references, a list of publications and annexes. The main material of the thesis has been presented over 92 pages featuring 20 tables and 52 pictures.

The defended statements of the thesis
1. After selecting the appropriate conditions (the molar ratio of the starting materials, the reaction time and temperature) between KCl and \( \text{NH}_4\text{H}_2\text{PO}_4 \) via conversion reaction, high-quality potassium dihydrogen phosphate may be obtained.
2. By using microcellulose, potassium dihydrogen phosphate obtained via conversion may be granulated with a drum granulator thus improving its properties (reducing hygroscopicity and increasing the amount of saleable fractions and the strength of granules).
3. By employing the mother liquid obtained in the process of conversion, a liquid NPK fertilizer may be produced thus ensuring waste-free production of potassium dihydrogen phosphate.
2. EXPERIMENTAL PART

Materials used in this work were chemically pure substances of potassium chloride (KCl, 99–100.5 % Sigma–Aldrich), ammonium dihydrophosphate (NH₄H₂PO₄, 99.0 % Fluka Analytical), ammonium nitrate (NH₄NO₃, 99.0 % Sigma–Aldrich), urea (CO(NH₂)₂, 99.05 % Sigma–Aldrich) and distilled water. The conversion reaction between potassium chloride and ammonium dihydrophosphate was analyzed by the determination of balance between liquid and solid phases in series of isomolar solutions. Aqueous solutions of these salts were prepared by dissolving starting materials, namely, potassium chloride and ammonium dihydrophosphate in the following molar ratios: 0.8:0.2; 0.6:0.4; 0.5:0.5; 0.4:0.6; 0.2:0.8. In each experiment, the total amount of salt is 5.5 mol, and 200 cm³ of distilled water was used. It was judged that equilibrium was reached after 5 hours as, after that period of time, the refractive index of the liquid fraction reached its final value and any changes ceased. The solid phase was obtained by filtering the mixture through a vacuum glass filter and dried in a drying stove.

The chemical composition of liquid and crystallized solid phases was analyzed by employing methods of chemical analysis: concentration of ammonium nitrogen (NH₄⁺) was established by the Kjeldahl method (Vapodest 45s); the concentration of phosphorus (P₂O₅) was determined by using the photocolorimetric method (T70/T80 UV–VIS); the concentration of chlorine (Cl⁻) was found out by employing the potentiometric method with the use of silver nitrate (“Titroline alpha plus”); the concentration of potassium (K₂O) was discovered by employing the marginal solutions method using the flame photometer “PFP–7.”

The chemical composition of the crystalline solid phase was analyzed by the diffraction analysis of Roentgen rays using the X–ray diffractometer “DRON–6” for CuKα radiation. The following settings were used: nickel filter; 0.02° movement step of detector; 0.5 s duration of intensity measurement in the step; 30 kV voltage; 20 Ma power of current; angle from 3° to 70°; rotation angle 2θ. The substances were identified by a computer using the “PDF–2 DATA” database.

FTIR analysis was performed with the spectrometer “Perkin Elmer FT–IR System.” The tablet pressed in the press form was used for the analysis (1 mg of substance mixed with 200 mg KBr). The analysis was implemented in the main range of the IR spectrum from 400 to 4000 cm⁻¹.

Differential scanning calorimetry was performed by using “Netzsch DSC214 Polyma” thermal analyzer and setting the following parameters: 10 °C/min temperature-raising speed, 25–300 °C temperature range, with weights of standard–blank Al crucible furnace atmosphere air samples equaling 13 mg.
For scanning electron microscopy (SEM), the FEI Quanta 200 FEG electronic microscope was used at magnification rates from 10 to 500,000.

The optical microphotographs were taken on the optical-biological microscope “Leica DM500.” 1 g of the crystalline solid phase was placed on a glass plate, and then a few drops of water were added.

Densities in the present study were measured by using the same weighing method under the same conditions for each liquid solution. Other properties (viscosity, pH) of the liquid solutions were measured by employing standard physical-chemical methods and using, respectively, the capillary Ostwald viscometer tube “VPZ–2” (capillary section size 1.31 mm) and the pH–meter “HANNA instruments pH 211” with the glass electrode HI1131B. The refractive index was measured by using a refractometer.

The crystallization temperature was measured by employing the cryoscopic polythermal method and using a mixture of ice, sodium chloride and ammonium chloride as a freezing agent. The crystallization temperature was measured with a mercury thermometer with the precision of 0.1 °C.

The corrosive power of solutions was measured by immersing stainless steel and carbon steel plates into solutions for 780 hours and then washing, drying and weighing them in order to establish the weight loss. The index of the corrosion depth was calculated by presuming that the sample undergoes corrosion to the same extent throughout the entire surface area.

The agrochemical assessment of the liquid complex fertilizer (4–5–15) was conducted by employing the method of modified micro-vegetative experiments. The experiment was conducted in plastic vessels filled with the same amount of mildly alkaline sandy loam soil. Into each vessel, 16 pre-sprouted seeds of summer wheat and barley were planted. For the lightning, artificial 1000 lx light of daylight lamps was used. The wheat and the barley were being grown until the sprouts started turning yellow because of almost exhaustive consumption of the nutrients (2 weeks).

Fertilizers were granulated in the laboratory drum-type granulator-dryer at 5 degrees of tilt angle and a constant (27 rpm) rotation speed. The raw materials were supplied to the granulator preheated up to 55–65 °C, the hot air was supplied for drying the granules into the drum-type granulator by air fan. For irrigation, tap water was used, which was being injected into the raw material mixture upstream of the drum-type granulator-dryer. By using the potassium dihydrogen phosphate (fraction < 1 mm), samples were granulated in the laboratory granulator (samples 1 to 21). To aid granulation, either MC–1 (Pharmacological Micro Cellulose) or MC–2 (Chromatographical Micro Cellulose) was used. The resultant granules were dried in an oven from 8 to 16 hours at 60 °C, and then their physical and chemical properties were assessed. Granulated fertilizer PDP was fractioned by using RETSCH-made woven sieves, and the shares of fractions (%) were determined by weighing them with
electronic scales (weighing precision of 0.001 g). The measurement of the amount of moisture was performed with the electronic moisture analyzer HG53. It utilizes the thermogravimetric principle, i.e. its activity is based on the decrease of weight under heating until the sample reaches the final stable weight. The static strength of granules was determined by using the IPG-2 device. The measurement range of 5–200 N was used, whereas the margin of error was ±2.00 % from the upper limit of measurement (when the temperature is 20±5 °C). The calculations were made by using standard methodology.

The TA.XT plus Texture Analyzer from Stable Micro Systems Ltd (Godalming, UK) was used in order to characterize the stiffness and strength of the granules. Individual granules were loaded at a constant test speed of 0.01 mm/s with a cylindrical stainless steel tool (5 mm in diameter) up to the deformation extent of 0.3 mm. The step motor used for the positioning of the tool had a distance resolution of 0.001 mm. The force necessary to drive the tool into the sample at a constant speed was recorded by a load cell (capacity: 50 N, accuracy: 5 mN). Once the threshold force (0.05 N) was exceeded, the data from the load cell was recorded at a frequency of 10 Hz in order to obtain the force–displacement curve.

3. RESULTS AND DISCUSSION

3.1 Dependence of Potassium Dihydrophosphate Yield on the Temperature and the Ratio of Potassium Chloride and Ammonium Phosphate

The equilibrium of potassium chloride and ammonium dihydrophosphate solid and liquid phases was analyzed under isothermal conditions at temperatures of 20, 40, 60 and 80 °C degrees. The solid phase was obtained when carrying out a conversion reaction between potassium chloride and ammonium dihydrophosphate:

\[ KCl_{(aq)} + NH_4H_2PO_4_{(aq)} \leftrightarrow KH_2PO_4_{(s)} + NH_4Cl_{(aq)} \]

The equilibrium between the solid and liquid phases was observed by measuring the refractive index which stabilized when the final equilibrium had been reached.

The phases were separated from each other by filtering through the Buchner filter and analyzed by employing the chemical and instrumental analysis methods. The chemical composition of the solid phase determined with chemical methods is presented in Table 3.1.

These results indicate that the composition of the solid phase is only moderately influenced by temperature. Going from 20 °C to 80 °C, the solid phase composition at the molar ratio of 0.8:0.2 changed as follows: the nitrogen
concentration increased from 1.69 % to 1.89 %, the phosphorus amount increased from 21.06 % to 21.66 % (except for the solid phase obtained at 80 °C temperature), the potassium levels increased from 29.14 % to 33.40 %, and chlorine decreased from 5.01 % to 1.87 %. The data in Table 3.1 shows that, at 60 °C, the chemical composition of the obtained solid phase is similar to that of pure potassium dihydrogen phosphate since the major part is made up of potassium (28.67 %) and phosphorus (22.79 %), and there are only traces of nitrogen and chlorine remaining. The high concentration of potassium and phosphorus, and the low concentration of ammonium and chlorine in the solid phase also occurs at 20–80 °C.

**Table 3.1. Concentration of the nutrients in the solid phase**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>The molar ratio of the starting materials, mol. r</th>
<th>Concentration of the nutrients in the solid phase*, %</th>
<th>Conc. of Cl, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KCl</td>
<td>NH₄H₂PO₄</td>
<td>N</td>
</tr>
<tr>
<td>20</td>
<td>0.8</td>
<td>0.2</td>
<td>1.69</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>2.60</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>4.05</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.6</td>
<td>6.38</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>11.10</td>
</tr>
<tr>
<td>40</td>
<td>0.8</td>
<td>0.2</td>
<td>1.82</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>1.96</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>3.86</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.6</td>
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</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>10.29</td>
</tr>
<tr>
<td>60</td>
<td>0.8</td>
<td>0.2</td>
<td>1.89</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
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<td>0.8</td>
<td>10.21</td>
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<td>80</td>
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<td>0.58</td>
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<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>1.89</td>
</tr>
<tr>
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<td>0.5</td>
<td>0.5</td>
<td>4.41</td>
</tr>
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<td>0.6</td>
<td>6.97</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>10.18</td>
</tr>
</tbody>
</table>

* – O and H in the solid phase made percentages up to 100 %;
** – P recalculated into P₂O₅ according to the fertilizer regulations;
*** – K recalculated into K₂O according to the fertilizer regulations.

High concentrations of potassium and phosphorus were obtained in the solid fraction, and the concentrations of nitrogen were low. Therefore, it can be stated that in order to obtain potassium dihydrophosphate, this molar ratio would be most suitable, as it corresponds to the stoichiometric ratio, according to which, the exchange reaction between potassium chloride and ammonium dihydrophosphate was carried out.
On the basis of the data acquired by performing the X-ray analysis (Figure 3.1), it would be safe to claim that all the diffractograms show most of the peaks that are characteristic to pure potassium dihydrogen phosphate (d = 0.509; 0.372; 0.301; 0.291; 0.263; 0.254; 0.235; 0.198; 0.195; 0.174; 0.166; 0.156 nm).

**Figure 3.1.** The XRD analysis curves of the solid phase performed at temperatures: a – 40 ºC; b – 60 ºC; A – KH₂PO₄, B – KCl, C – NH₄Cl, D – NH₄H₂PO₄, E – K₂HPO₄

In the case when the molar ratio between potassium chloride and ammonium dihydrogen phosphate was 0.8:0.2 and the temperature was 40 ºC (Figure 3.1, a, 2 curves), the composition of the solid phase was closest to that of pure potassium dihydrogen phosphate (Figure 3.1, a, 1 curve). The peaks of the solid phase obtained at 40 ºC conversion temperature when the molar ratio KCl:NH₄H₂PO₄ is equal to 0.6:0.4; 0.5:0.5; 0.4:0.6; 0.2:0.8 (Figure 3.1, a, 3–6 curves) hardly differs from the peaks of pure potassium dihydrogen phosphate. Moreover, several low intensity peaks were identified which can be attributed to KCl (d = 0.315 nm), NH₄Cl (d = 0.157 nm), and NH₄H₂PO₄ (d = 0.169 nm). The identification of this starting material supports the results of chemical analysis as it shows a small amount of Cl⁻ found in the solid phase.
At the conversion temperature increased to 60 °C (Figure 3.1, b), the composition of the solid phase was obtained. The X-ray diffractograms when the molar ratio KCl:NH₄H₂PO₄ was equal to 0.8:0.2 and 0.6:0.4 (Figure 3.1, b, 2 and 3 curves) shows that most of the peaks are characteristic to pure potassium dihydrogen phosphate (Figure 3.1, b, 1 curve).

At 60 °C and with the molar ratio between potassium chloride and ammonium dihydrogen phosphate being 0.5:0.5 and 0.4:0.6 (Figure 3.1, b, 4 and 5 curves.), X-ray shows peaks characteristic of KH₂PO₄, KCl, NH₄Cl and NH₄H₂PO₄. At the same temperature, when KCl:NH₄H₂PO₄ = 0.2:0.8 (Figure 3.1, b, 6 curve) reduces the peaks characteristic of KH₂PO₄ but increases the intense peaks characteristic of NH₄H₂PO₄ (d = 0.533; 0.376; 0.201; 0.169 nm) and NH₄Cl (d = 0.272 nm).

To sum up, X-ray data confirms the results of the chemical analysis. At 40 °C and 60 °C temperatures and at the potassium chloride and ammonium dihydrogen phosphate molar ratio 0.8:0.2 and 0.6:0.4, the solid phase is formed nearly of pure potassium dihydrogen phosphate (PDP). The identification peaks of KCl, NH₄Cl and NH₄H₂PO₄ suggest that in the solid phase there are small amounts of nitrogen and chlorine additions.

![Figure 3.2. IR spectra of the solid phase obtained during conversion when the molar ratios of KCl and NH₄H₂PO₄ were respectively: a – 0.8:0.2 and b – 0.6:0.4](image-url)
IR spectra (Figure 3.2) were recorded in order to analyze the obtained solid phases in more detail. They show that the spectrum of the solid phase resulting in the conversion temperature of 60 °C and KCl:NH₄H₂PO₄ = 0.8:0.2 (Figure 3.2, a, 2 curve) is not significantly different from that of pure KH₂PO₄. According to the information presented in scholarly literature, the wavelength of ~2500–3500 cm⁻¹ is usually attributed to –OH. However, the vibrations in this area (3129.66 cm⁻¹ and 3125.52 cm⁻¹) can also be attributed to N–H or NH₄⁺ functional groups. The solid phase IR spectrum (Figure 3.2, a, 3 curve) (40 °C conversion temperature and KCl:NH₄H₂PO₄ = 0.8:0.2) peak corresponding to 1453.00 cm⁻¹ wave number can be attributed to the functional group NH₄⁺.

IR spectra in Figure 3.2, b, 2 and 3 curves show absorption band doublets within the portion of 3129.3–3251.76 cm⁻¹ of the spectrum, and these doublets can be attributed to valence vibrations of the NH₄⁺ ion. This confirms the presence of inorganic salts in the obtained solid phase. In accordance with the data of Jegatheesan et al., the vibrations in the spectrum part 1658.17–1718.90 cm⁻¹ can be attributed to the –OH group. Considering the studies presented in the same paper, it can be stated that the peaks of the absorption bands in the 1404.07–1453.89 cm⁻¹ part are specific to valence vibrations of the PO₄³⁻ ion. The doublets of the absorption bands in the 909.54–1102.27 cm⁻¹ part of all the spectra can be attributed to valence vibrations of the PO₄³⁻ functional group. In addition, the peaks of the absorption bands beside the 539.74–663.82 cm⁻¹ part of the spectrum can be attributed to valence vibrations of the tetrahedral form of PO₄³⁻. As Figure 3.2 demonstrates, in all the cases, the spikes of the absorption bands did not change their location position. Subject to these vibrations, it can be stated that inorganic salt of KH₂PO₄ is present in the obtained solid phases. The differences between the spectra of solid phases obtained during conversions and presented in Figure 3.2 and the IR spectrum of pure potassium dihydrogen phosphate (Fig. 3.2 a, 2 curve) are not significant.

The SEM of the solid phases was performed, and the results are presented in Figure 3.3.

![Figure 3.3](image-url)  
*Figure 3.3. SEM of a – pure KH₂PO₄ and of the solid phase when the molar ratio of KCl and NH₄H₂PO₄ is equal to 0.8:0.2 performed at temperatures: b – 20 °C; c – 40 °C; d – 60 °C; e – 80 °C*
The images demonstrate that the crystals of the synthesized material at 20 °C and 40 °C (Figure 3.3 b–c) are somewhat reminiscent of the crystals of pure potassium dihydrogen phosphate by their surface and shape (Figure 3.3 a). Meanwhile, the solid phases obtained during the conversion reactions between potassium chloride and ammonium phosphate at 60 °C and 80 °C (Figure 3.3 d and e) are very similar to pure potassium dihydrogen phosphate in terms of the surface and particle shape.

The purity of the PDP (synthesized potassium dihydrogen phosphate) may be assessed by performing measurements of the dependence of the heat capacity on temperature (Figure 3.4).

![Figure 3.4. Dependence of the heat capacity on temperature: a – KH₂PO₄; b – PDP; c – NH₄Cl; d – KCl; e – NH₄H₂PO₄](image)

It was established that when the molar ratio between potassium chloride and ammonium dihydrogen phosphate was 0.8:0.2, then, at 40 °C and 60 °C, the equilibrium solid phase was chemically highly similar to pure KH₂PO₄. When the conversion reaction temperature was increased to 60 °C, the resulting substance by its chemical composition and the “appearance” was virtually identical to pure potassium dihydrogen phosphate.

![Figure 3.5. The product obtained after the conversion reaction between KCl and NH₄H₂PO₄ at 60 °C temperature – crystalline PDP](image)
Conversion of potassium chloride and ammonium dihydrophosphate occurred at the temperature of 60 °C, when the molar ratio of the source materials was 0.8:0.2, and potassium dihydrophosphate was the result. This crystallized product may be used directly as potassium and phosphorus fertilizer. Alternatively, it could be used in the production of NPK fertilizers.

The results of the experiments may be summed up as follows: the best conditions for the processing of PDP via conversion and the main physical-chemical properties of the product (PDP) obtained under the outlined conditions were as follows:

- the molar ratio of the source materials (KCl and NH₄H₂PO₄) was 0.8:0.2;
- the conversion temperature was 60 °C;
- the obtained product was in the form of crystals of various sizes, PDP;
- the concentration of the nutrients in the product was as follows: 21.66 % (49.67 %) – phosphorus (recalculated into P₂O₅); 32.27 % (38.08 %) – potassium (recalculated into K₂O); 1.89 % – nitrogen; 1.87 % – chlorine;
- pH of 10 % solution was 3.8;
- moisture (after filtering) was 17–20 %.
- moisture (after drying) was 3.3 %.

3.2 Granulation of Potassium Dihydrogen Phosphate

In order to determine the optimal parameters of the granulation process (the composition of the raw material, the particle size, the moisture content) of various organic materials (microcrystalline cellulosics of either MC–1 or MC–2 kinds) suitable for production of high quality fertilizers, various mixtures of raw materials were granulated in laboratory conditions. Potassium dihydrogen phosphate was granulated by using 3 granulators of different types: rotary, a fluidized bed and a drum. Potassium phosphate granulation was investigated by changing the amount of water used for irrigation purposes as well as by adding a binder (cellulose). According to the obtained results, the fluidized bed and rotary granulators cannot be used to obtain granulated mono potassium phosphate as the granulometric composition does not meet the necessary fertilizer requirements.

Granules (as a product) obtained from the rotary drum-type granulator were dried for approximately 16 hours in the heating oven at 60 °C. All the samples were cooled and fractioned, and then, the granulometric composition, the granule moisture and bulk were determined. The static strengths of granules of 1–2 and 2–3.15 mm fractions and the 10 % solution pH values were measured. The results of the first 7 granulated samples are presented in Table 3.2.
Table 3.2. Physico-chemical properties of granulated PDP with water

<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>Raw material moisture, %</th>
<th>Granulometric composition, %</th>
<th>Granule moisture, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>&lt;1 mm</td>
<td>1–2 mm</td>
</tr>
<tr>
<td>1</td>
<td>10.08</td>
<td>94.8</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>15.09</td>
<td>88.63</td>
<td>8.32</td>
</tr>
<tr>
<td>3</td>
<td>17.50</td>
<td>87.20</td>
<td>7.21</td>
</tr>
<tr>
<td>4</td>
<td>21.02</td>
<td>58.83</td>
<td>18.47</td>
</tr>
<tr>
<td>5</td>
<td>22.50</td>
<td>91.19</td>
<td>2.86</td>
</tr>
<tr>
<td>6</td>
<td>26.85</td>
<td>87.10</td>
<td>3.4</td>
</tr>
<tr>
<td>7</td>
<td>30.21</td>
<td>83.85</td>
<td>6.15</td>
</tr>
</tbody>
</table>

With 21.02 % moisture being present in the source materials, the obtained granulated product was denoted by the optimal granulometric composition (Sample 4) as its commodity fraction constitutes 40.54 %. Hence this sample was investigated while striving to establish other properties of compound fertilizers: pH of 10 % solution, 1–2 mm and 2–3.15 mm diameter granule static strength, bulk (freely poured and densified) density and the Stokes criterion (Table 3.2)

Table 3.3. Parameters of product granulated only with water

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Diameter of granules</th>
<th>pH (10% solution)</th>
<th>Strength, N/gran.</th>
<th>Bulk density of granules, kg/m³</th>
<th>Stokes criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1–2 mm</td>
<td>3.7</td>
<td>7.27⁺</td>
<td>778</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>2–3.15 mm</td>
<td>3.7</td>
<td>7.25**</td>
<td>765</td>
<td>0.03</td>
</tr>
</tbody>
</table>

* – $S_x = 1.62$, $\delta_x = 0.76$, $\Delta = 0.0052$;

** – $S_x = 2.14$, $\delta_x = 1.00$, $\Delta = 0.0072$.

From the presented data, it is evident that the static strength of the pellets is relatively low (7.3 N/gran.), and that the 10 % fertilizer solution is acidic. The bulk density of the pellets is lower than the critical value; this means that the formation of pellets was caused by the adhesion and growth of the particles of the source material.

In order to explore the properties (Figure 3.6) of granulated PDP in greater detail, TA.XT plus Texture Analyzer with Exponent software was employed to research the distribution of 2–3.15 mm granules in the sample (50 granules of either size category were used).
Figure 3.6. Properties of granules (2–3.15 mm) of the granulated product, which was obtained only by water potassium dihydrogen phosphate wetting. Distribution by:

- \( a \) – diameter;
- \( b \) – weight;
- \( c \) – breakage force;
- \( d \) – compressibility

Analysis of the distribution of granulated PDP in terms of size (Figure 3.6 \( a \)) shows that the 2–3.15 mm fraction features 40 % units of ~2.3 mm sized pellets. In the different fractions, the prevalent diameter of the pellets differs by ~0.8 mm. The weight of the pellets (Figure 3.6 \( b \)), depending on their size in the 2–3.15 mm fraction, ranges from 5.7 mg to ~28 mg. In the bulkier fraction, ~11 mg weighing pellets predominate.

Pellet uniformity assessment was made by taking fertilizer photos while using optical and scanning electron microscopy techniques. The obtained photos are presented in Figure 3.7.

Figure 3.7. SEM photos of a product, granulated only with water (no microcrystalline cellulose) with different magnifications: \( a \) – \( \times500 \); \( b \) – \( \times700 \); \( c \) – \( \times1000 \)
The obtained results indicate that in order to obtain granulated potassium dihydrophosphate with optimal properties, the use of water does not suffice. It is also necessary to use other additives in order to improve the physical and mechanical properties of the pellets. Analysis of scholarly writings on the binding materials used in the granulation technology suggests that if the objective is to obtain maximally pure potassium dihydrophosphate, cellulose should be chosen as the binder as it contains no additional nutrients consumed by plants. In addition, cellulose is denoted by its cohesion properties.

Micro-crystalline cellulose (commonly used in pharmaceutical applications) was used for granulation. The synthesized potassium dihydrophosphate was granulated by using water and cellulose as a binding material.

Data on the use of cellulose as the binding material and employing water as the moisturizer is presented in the Table 3.4.

**Table 3.4. Physico-chemical properties of granulated PDP with MC–1 and water**

<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>Granulation conditions</th>
<th>Granulometric composition, %</th>
<th>Gran. moisture, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Moisture content in the raw m., %</td>
<td>Cellulose content in the raw m., %</td>
<td>&lt;1 mm</td>
</tr>
<tr>
<td>8</td>
<td>21.08</td>
<td>1</td>
<td>51.52</td>
</tr>
<tr>
<td>9</td>
<td>21.14</td>
<td>2</td>
<td>33.37</td>
</tr>
<tr>
<td>10</td>
<td>21.49</td>
<td>5</td>
<td>20.11</td>
</tr>
</tbody>
</table>

From the data presented in Table 3.4, it is evident that cellulose as an additive greatly improves the granulometric composition of potassium dihydrophosphate. When using the same amount of moisture and ~1 % MC–1, ~47 % commodity fraction is yielded whereas the increase of MC–1 up to ~2 %, correspondingly, ~58 % of the commodity fraction is obtained. The granulated product with the best granulometric composition is obtained when ~5 % MC–1 is used, and 71.86 % of the commodity fraction is yielded (Sample 10).

**Table 3.5. Parameters of product granulated with FMC and water**

<table>
<thead>
<tr>
<th>Sample Nr.</th>
<th>Diameter of granules</th>
<th>pH (10% solution)</th>
<th>Strength, N/gran.</th>
<th>Bulk density of granules, kg/m³</th>
<th>Stokes criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>bulk</td>
<td>multiplexed</td>
</tr>
<tr>
<td>10</td>
<td>1–2 mm</td>
<td>4.25</td>
<td>7.38</td>
<td>785</td>
<td>810</td>
</tr>
<tr>
<td></td>
<td>2–3.15 mm</td>
<td>4.25</td>
<td>7.32**</td>
<td>770</td>
<td>790</td>
</tr>
</tbody>
</table>

* $S_x = 2.48, \delta_x = \pm 1.16, \Delta = 0.0078$;

** $S_x = 2.38, \delta_x = \pm 1.11, \Delta = 0.0076$.

According to the established granulometric composition, upon selecting the optimal type of granulation, the static strength, the bulk (freely poured and densified) density of the sample (1–2 mm and 2–3.15 mm diameter granules), and pH of 10 % solution was established; the Stokes criterion was also calculated. In order to further analyze the granular PDP properties, TA.XT Plus

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Texture Analyzer software “Exponent” was used to study the 2–3.15 mm diameter fraction and the particle distribution of the sample (the sample size was 50 beads) (Figure 3.8).

![Graphs showing granule properties](image)

**Figure 3.8.** Properties of the granules (2–3.15 mm) of the granular product which was obtained by wetting potassium dihydrogen phosphate with water and adding 5 % MC–1. Distribution by: a – diameter; b – weight; c – breakage force; d – compressibility

Granule uniformity was assessed by using fertilizer photos obtained by employing optical and scanning electron microscopy techniques which are presented in Figure 3.9.

![SEM photos](image)

**Figure 3.9.** SEM photos of product granulated with MC–1 and water with different magnification: a – ×200; b – ×500; c – ×1000

From the photos presented in Figure 3.9, it is evident that when pharmaceutical grade cellulose was used for granulation, more spherical-shaped pellets were formed in comparison to the pellets formed when granulating with water only.

While the use of MC–1 improves the properties of the granulated product as measured by granulometric composition and pH, it does not increase the pellet
strength. Also, MC–1 does not distribute throughout the pellet consistently. For these reasons, cellulose of a different type was tried.

The microcrystalline cellulose of a different kind (MC–2) was selected. A possible advantage of using MC–2 is that it is slightly cheaper. Data on the use of cellulose as the binding material and employing water as the moisturizer is presented in Table 3.6.

Table 3.6. The physico-chemical properties of granulated PDP with MC–2 and water

<table>
<thead>
<tr>
<th>Sam. No.</th>
<th>Diameter of granules</th>
<th>pH (10% solution)</th>
<th>Strength, N/gran.</th>
<th>Bulk density of granules, kg/m³</th>
<th>Stokes criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>1–2 mm</td>
<td>3.89</td>
<td>9.22*</td>
<td>810</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>2–3.15 mm</td>
<td>3.89</td>
<td>8.24**</td>
<td>770</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* $S_x = 2.40$, $\delta_x = 1.12$, $\Delta = 0.0061$;
** $S_x = 2.54$, $\delta_x = 1.18$, $\Delta = 0.0072$.

In order to further analyze the granular PDP properties, TA.XT Plus Texture Analyzer software “Exponent” was used to study the 2–3.15 mm diameter fraction. The sample article distribution in the sample (the sample size was 50 beads) is presented in Figure 3.10.

All the samples were cooled and fractioned. Then granulomeric compositions and SGN were determined, static strengths of granules of 1–3.15 mm fractions and 10% solution pH values were measured. These results of the granulated samples are presented in Table 3.7.

Table 3.7. Parameters of a product granulated with MC–2 and water

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Diameter of granules</th>
<th>pH (10% solution)</th>
<th>Strength, N/gran.</th>
<th>Bulk density of granules, kg/m³</th>
<th>Stokes criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1–2 mm</td>
<td>3.89</td>
<td>9.22*</td>
<td>810</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>2–3.15 mm</td>
<td>3.89</td>
<td>8.24**</td>
<td>770</td>
<td>0.04</td>
</tr>
</tbody>
</table>
Figure 3.10. Properties of the granules (2–3.15 mm) of the granulated product which was obtained by wetting potassium dihydrogen phosphate with water and adding 5 % MC–2.

Distribution by: a – diameter; b – weight; c – breakage force; d – compressibility

Pellet uniformity was assessed by taking photos with a scanning electron microscope. The obtained photos are presented in Figure 3.11.

Figure. 3.11. SEM photos of a product granulated with MC–2 and water with different magnification: a – ×200; b – ×500; c – ×1000

The hygroscopicity of the pellets was measured by observing the alterations of the weight of the fertilizer sample when water vapor adsorption was taking place in 1–2 mm and 2–3.15 mm-sized pellets.

3.3. Liquid Compound Fertilizers

After the reaction with potassium chloride and ammonium dihydrophosphate and the removal of solid potassium dihydrophosphate, the liquid fraction is left.

We may wonder whether this by-product liquid fraction could be of use as a
fertilizer. The chemical composition of the liquid phase determined by chemical methods is presented in Table 3.8.

**Table 3.8.** Concentration of the nutrients in the solid phase

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>The molar ratio of the starting materials mol. r.</th>
<th>Concentrations of the nutrient in the liquid phase*, %</th>
<th>Conc. of Cl, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KCl</td>
<td>NH₄H₂PO₄</td>
<td>N</td>
</tr>
<tr>
<td>20</td>
<td>0.8</td>
<td>0.2</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>2.82</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.6</td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>3.15</td>
</tr>
<tr>
<td>40</td>
<td>0.8</td>
<td>0.2</td>
<td>1.25</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>2.57</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.6</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>2.98</td>
</tr>
<tr>
<td>60</td>
<td>0.8</td>
<td>0.2</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>2.69</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.6</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>3.19</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
<td>0.2</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>0.4</td>
<td>2.65</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>2.93</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>0.6</td>
<td>3.05</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.8</td>
<td>3.09</td>
</tr>
</tbody>
</table>

*– up to 100 % other elements present in the solid state (O, H);
** – P recalculated into P₂O₅ according to the fertilizer regulations;
*** – K recalculated into K₂O according to the fertilizer regulations.

The composition of the liquid phase at 60 °C temperature changes in the following way: the concentration of nitrogen increases from 1.39 % to 3.19 %, the concentration of phosphorus increases from 1.11 % to 5.31 %, the concentration of potassium decreases from 14.96 % to 1.64 %, and the concentration of chlorine also decreases from 13.71 % to 1.85 %. Therefore, under these conditions, the conversion of primary materials produces the best results.

In order to increase the nitrogen concentration in liquid solutions, ammonium nitrate and urea were used. The test of the crystallization temperature was determined by cryoscopy, by using the polythermal method. The solubility in the temperature range from 5 °C to 25 °C was investigated as the solutions were cooled until crystallization occurred and then warmed very slowly with continuous stirring, until the last crystals disappeared. A series of solutions at different concentrations of NH₄NO₃(s) and CO(NH₂)₂(s) were cooled, and at a certain temperature, crystals formed in each solution as a result. In order to
increase the nitrogen concentration and to lower the crystallization temperature, CO(NH$_2$)$_2$ and NH$_4$NO$_3$ were tried out.

For solutions to be used as LCF, it is necessary to determine their crystallization temperature. As nitrogen concentration was very low in the starting solutions, urea was tried to amend that deficiency. The polytherm of crystallization of the liquid solutions, obtained during the conversion reaction at temperatures of 20 ºC, 40 ºC, 60 ºC, 80 ºC with different concentrations of urea was investigated (Figure 3.12).

![Figure 3.12](image)

**Figure 3.12.** The crystallization polytherm of the liquid solutions obtained during the conversion reaction at temperatures of $a$ – 20 ºC, $b$ – 40 ºC, $c$ – 60 ºC, $d$ – 80 ºC. Optical microscopic image of powder solid phase

All polytherms followed the classical polytherm shape. They had only one eutectic (breaking) point, which shows the lowest temperature of crystallization under certain concentration of urea.

As it can be seen in the picture (Figure 3.12, $a$) the temperature of crystallization was the lowest (13.5 ºC) at 6 % of CO(NH$_2$)$_2$ concentration. Accordingly, the crystallization temperature is 15 ºC, and the concentration of CO(NH$_2$)$_2$ is 6 % in Figure 3.12, $b$; 15 ºC and 6 % in Figure 3.12, $c$; 13 ºC and 5 % in Figure 3.12, $d$. In each part of the polytherm, before and after the eutectic
point, a different solid phase crystallized whose chemical composition was subsequently investigated.

Viscosity, pH and density values are very important in selecting equipment for liquid compound fertilizer production and use (Figure 3.13).

Therefore, density, pH and viscosity of liquid solutions (LS), obtained during the conversion reaction at different temperatures while adding CO(NH$_2$)$_2$ was determined. It can be stated that with the increased concentration of urea, the viscosity, pH and density increased, too. As it can be seen in the picture (Figure 3.14, $a$), the temperature of crystallization was the lowest (4 °C) at 7 % of NH$_4$NO$_3$ concentration. Accordingly, the crystallization temperature is 6 °C, and the concentration of NH$_4$NO$_3$ is 8 % in Figure 3.14, $b$; 5 °C and 8.3 % in Figure 3.14, $c$; 5 °C and 7 % in Figure 3.14, $d$. In each part of the polytherm before and after the eutectic point, a different solid phase crystallized whose chemical composition was investigated. The solid phase with 2 % and 14 % ammonium nitrate obtained during crystallization was analyzed by using chemical methods of analysis.
Figure 3.14. The crystallization polytherm of the liquid solutions obtained during the conversion reaction at temperatures of $a - 20 \degree C$, $b - 40 \degree C$, $c - 60 \degree C$, $d - 80 \degree C$. Images of the powder solid phase were obtained by employing optical microscopy.

Density, pH and viscosity values are extremely important in selecting equipment for LCF production and use (Figure 3.15). Therefore, viscosity and density of liquid solutions (LS) obtained during the conversion reaction at different temperatures with NH$_4$NO$_3$ being added was determined. It can be stated that with the increased concentration of NH$_4$NO$_3$, the viscosity and density increased, too.
Figure 3.15. Density (a), pH (b) and viscosity (c) of liquid solutions obtained during the conversion reaction at different temperatures (ºC):♦ – 20 ºC; ■ – 40 ºC, ▲ – 60 ºC; ● – 80 ºC while adding NH₄NO₃

With the increase of the NH₄NO₃ concentration, pH changes independently of the conversion temperature and varies from 3.61 to 4.31. Such solutions are classified as weakly corrosive as they can corrode iron or steel but not stainless steel.

Assessment of the properties of the liquid by-product fraction (chemical composition, temperature of crystallization, pH, density and viscosity) led to the conclusion that the solution which remains after the conversion at a temperature of 60 ºC and includes 8 % of NH₄NO₃ is the most appropriate liquid solution to be used for the production of LCF. Corrosivity studies were performed by using this liquid and testing carbon and stainless steels (Figure 3.16). The measurements were performed by measuring the mass change.

Figure 3.16. The corrosivity of the steels in the liquid solutions obtained during the conversion reaction at 60 ºC temperature with 8 % NH₄NO₃: ■ – carbon steel (ST3); ♦ – stainless steel (35S22099)
It was determined that carbon steel corroded and stainless steel did not. This fact confirmed the data in the scholarly literature about the influence of LCF pH on steel alloys. The biggest corrosion depth index (6.8 mm/year) of corrosivity to carbon steel was observed during the first 5 hour period.

The agrochemical assessment of the produced liquid complex fertilizer was performed by conducting micro-vegetation tests which yielded conclusions on the absorption of the nutrients contained in the fertilizer and its impact on the plants. Spring triticale and barley were selected for the research as the obtained liquid potassium fertilizer is more appropriate for fertilizing field plants in summer.

Having considered the nutritional materials contained in the explored liquid fertilizer, the following pattern of experimentation was selected:

1. The mother liquid (obtained from the potassium chloride and ammonium dihydrophosphate reaction) with 6% of CO(NH$_2$)$_2$ (this is 4–5–15 fertilizer brand);
2. The mother liquid with 8% NH$_4$NO$_3$ (this is 4–5–15 fertilizer brand);
3. Without fertilizers (control test) (Figure 3.17).

![Figure 3.17. Comparison of the agrochemical test of the results when different liquid fertilizers for fertilization were used: 1: 4–12–15 (with CO(NH$_2$)$_2$); 2: 4–12–15 (with NH$_4$NO$_3$); 3: control test (without any fertilizer)](image)

As the results presented in Picture 3.17 evidently show, the largest share of the ‘dry crop’ (spring triticale and barley) and the highest mass of ash was obtained when the 4–5–15 brand LCF fertilizer containing ammonium nitrate was used. The lowest mass of the crops was obtained when they were not
fertilized at all (i.e. were sprinkled with water only). The composition of the fertilizer did not have any significant impact on the height of the leaves of the crop in any case as they were similar as long as some fertilizer was used (i.e. longer than the control sample that was sprinkled with water only).

3.4 Technological Recommendations for Potassium Dihydrogen Phosphate Production

The obtained results under laboratory conditions allow creating a production technology of compound fertilizers in the granulate form and determining the optimal technological parameters. The principal technological scheme is presented in Figure 3.18.

Figure 3.18. Technological scheme for the production of PDP: 1, 2 – bucket elevators; 3, 8, 10, 16, 18 – screw conveyors; 4, 12, 19 – sieves; 5, 13, 21 – dispensers; 6, 22 – mixing reactor; 7 – filter; 9, 17 – dryers; 11 – rotary mill; 14 – mixer; 15 – drum granulator; 20 – cooler; 23 – standartisator
KCl and NH₄H₂PO₄ are transported by the bucket elevator and the screw conveyor into the sieve. Raw materials are fractioned on the sieves where the fraction under the dispenser is supplied to the mixing reactor. The required amount of water is supplied to the mixing reactor where salts are dissolved and the conversion reaction is carried out. The reactor was heated with steam and added water (60 °C temperature). When the reaction ended, the solid phase (potassium dihydrogen phosphate) was filtered and tumble-dried while maintaining the temperature at 60 °C. Potassium dihydrogen phosphate was dried on the conveyor belt which carried it to the mill to be crushed and sieved. Granules larger than 1 mm in diameter were fractioned on the sieves, and the smallest fraction was returned to the mixer. Granules larger than 5 mm were crushed by hammer mill crusher and returned to the double-meshed sieves. In the sieves, a separate large-scale (>1 mm) fraction is returned to the mill grinding, and the small-scale (<1 mm) fraction is used for granulation in the mixer which is available as required for dispensing the cellulose content. The mixture is fed into the drum granulator which operates while maintaining temperature within the interval of 55–65 °C. The granulated product from the granulator is transferred to the belt conveyor dryer which is set at 60 °C. The dried potassium dihydrogen phosphate is sieved to be separated for the premium retail (1 to 3.15 mm) fraction, which then falls into the cooler and cools down to the ambient temperature (20–25 °C). The chilled product (PDP) is supplied to the warehouse. After sieving the remaining fine fraction (<1 mm), it is returned to the mixer and reused. The liquid by-product fraction is supplied to the reactor, where some urea or ammonium nitrate is added to improve its nitrogen content and to reduce the crystallization temperature.

4. CONCLUSIONS

1. It was found that the interaction of KCl and NH₄H₂PO₄ aqueous solution product which has the chemical composition of (49.7 % P₂O₅, 38.1 % K₂O) and K₂O:P₂O₅ ratio of (0.67 w/w) is the most suited for pure KH₂PO₄ composition (52.2 % P₂O₅; 34.6 % K₂O), and the ratio of (0.66 w/w) was obtained when the reaction time was 5 h, the temperature was 60 °C, and the molar ratio of the starting materials was 0.8:0.2.

2. It was determined that the best parameters of granular potassium dihydrogen phosphate (65 % marketable fractions, static strength of the granule – 8.73 N/gran.; moisture of the granule – 1.7 %) was obtained with the drum granulator when: the raw material mixture contained 5 % cellulose and 21 % humidity; the temperature was in the range of 55–65 °C; the rotation speed was 27 rpm. It was found that it is possible to produce the liquid fertilizer
4–5–15 grade in the post-crystallization of potassium dihydrogen phosphate remaining solution by adding 6 % of CO(NH₂)₂ or 8 % of NH₄NO₃ wherein the crystallization temperature was 15 °C or 6 °C.

3. Having performed agrochemical evaluation of the liquid potassium fertilizer 4–5–15 featuring urea or ammonium nitrate, it was discovered that the fertilizer sample featuring ammonium nitrate is more efficient. It increased the test plate dry weight by 68.4 %, the ash content by 62.7 % and the height of the plants by 43.5 %.

4. It was established that carbon steel (St3) is not suitable for the production, storage and application of a liquid compound fertilizer because its corrosion depth is denoted with a high index (6.81 mm/year). However, alloy steel (35S22099) may be used since corrosion regarding this type of steel was too slow to measure.

5. To sum up, the principal technological scheme and the basic parameters of granular potassium dihydrogen phosphate (49.7 % P₂O₅; 38.08 % K₂O; 1.9 % N and 1.9 % Cl) and the liquid composite 4–5–15 grade fertilizers were outlined.

LIST OF PUBLICATIONS AND PROCEEDINGS ON THE THEME OF DISSERTATION

Publications on the list of Clarivate Analytics Web of Science Database


Publications in Proceedings of Conferences


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REZIUME

Temos aktualumas

Pasaulyje nuolat didėjant žmonių populiacijai, tačiau nesiplečiant dirbamos žemės plotams, pakankamą maisto produktų kiekį ir kokybę galima užtikrinti tik intensyvinant žemdirbystę pasitelkus visas įmanomas priemones. Siekiant užtikrinti kuo didesnį įvairių žemės ūkio kultūrinių augalų derlingumą nuolat tobulinamos jau esamos trąšos ir jų gamybos technologijos bei kuriamos naujos trąšos ir ieškoma naujų jų gavimo būdų. Daug dėmesio skiriama atsinaujinančių išteklių, t. y. įvairios biosąs naudojimui žemės ūkioje, tačiau vien biosąs negali užtikrinti pilnavečio augalų aprūpinojo maisto medžiogomis, nes joje dažnai nebūna vieno ar kito augalams būtino elemento, o ir jų santykis būna nesubalansuotas, todėl dažnai turi būti koreguojamas atsižvelgiant į augalų rūšis, vegetacijos laikotarpį, klimatines sąlygas ir kt.

Vienas iš būdų trąšų poveikio padidinti yra gaminti didelės koncentracijos trąšas panaudojant tam kuo pigesnes žaliavas ir kuo paprastesnį gavimo būdą. Labai didelės koncentracijos, tačiau dėl naudojamų sudėtingų gamybos technologijų gana brangios trąšos yra kalio fosfatai (kalio hidrofosfatas ir kalio dihidrofosfatas). Dėl didelės kainos kalio dihidrofosfatas (KDF) dažniausiai naudojamas tik tiems augalams, kurie labai jautūs chloro poveikui, t. y. šiltimamiuose auginamoms gėlėms ir daržovėms.

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Kalo dihidrofosfato iš kalio chlorido ir amonio dihidrofosfato gavimo konversijos būdu duomenų nėra. Tokie tyrimai yra svarbūs, nes jų rezultatai leistų paprastui ir iš pigių žaliavų gaminti birias koncentruotas bechlorės fosforo fosforo kalio trąšas, bei sumažinti susidarančių atliekų kiekį, nes skystoje faze būtų
naudojama skystosioms trąšoms gaminti. Iš minėtų žaliavų pagamintas produktas būtų pigesnis, todėl galėtų būti naudojamas ne tik šiltamąjį, bet ir kitiems augalams tręsti.

Darbo tikslas ir uždaviniai

Darbo tikslas – nustatyti kalio dihidrofosfato gavimo vandeniniuose kalio chlorido ir amonio dihidrofosfato tirpaluose sąlygas ir pasiūlyti beatliekinę biriųjų fosforo kalio ir skystųjų azoto fosforo kalio trąšų gamybos principinę technologinę schemą.

Uždaviniai:
1. Nustatyti kalio chlorido ir amonio dihidrofosfato sąveikos vandeniniuose tirpaluose produktus ir parinkti geriausias kalio dihidrofosfato gavimo konversijos būdu sąlygas.
2. Išsiaiškinti ir įvertinti skirtingų granuliavimo būdu įtaką sugranuliuto kalio dihidrofosfato fizikinėms cheminėms savybėms ir parinkti tinkamiausią granuliavimo būdu bei geriausius proceso parametrus.
3. Išsiaiškinti konversijos metu susidariusios skystosios fazės sąveiką su karbamidu ir amonio nitratu, parinkti skystųjų kalio dihidrofosfato sudėtis ir įvertinti gauto produkto fizikines chemines savybes bei agrocheminį efektyvumą.
4. Sukurti principinę technologinę schemą granuliuotam kalio dihidrofosfatui ir skystosioms kompleksinėms azoto fosforo kalio trąšoms iš kalio chlorido ir amonio dihidrofosfato gaminti.

Mokslinis naujumas

1. Nustatyti pusiausvyros kalio chlorido ir amonio dihidrofosfato vandeniniuose tirpaluose parametrai ir parinktos geriausios sąlygos kalio dihidrofosfatui konversijos būdu gauti.
2. Sudarytos po kalio chlorido ir amonio dihidrofosfato sąveikos likusios skystosios fazės (pokristalizacinių tirpalų) fazių pusiausvyros diagramos, įvertinant karbamido bei amonio nitrato priedų įtaką.

Praktinė vertė

1. Įvertinus karbamido ir amonio nitrato sąveiką su pokristalizaciniu tirpalu sukurtos skystosios 4–5–15 markės NPK trąšos.
2. Pasiūlyta principinė technologinė schema granuliuotoms sudėtinėms PK trąšoms ir skystosioms NPK trąšoms gaminti.
Darbo aprobatavimas ir publikavimas

Disertacinio darbo tema paskelbtos 2 publikacijos su citavimo indeksu žurnaluose įtraukus didelęvieną publikaciją kituose recenzuojamuose leidiniuose, 5 publikacijos konferencijų medžiagoje ir kartu su bendraautoriais pateikta paraiška LR patentui gaun. 

Darbo apimtis

Disertaciją sudaro įvadas, literatūros duomenų analizė, metodinė dalis, tyrimų rezultatai ir jų apibendrinimas, išvados, 123 literatūros šaltinių sąrašas, publikacijų disertacijos tema sąrašas ir priedai. Pagrindinė medžiaga išdėstyta 92 puslapyje, įskaitant 20 lentelių ir 52 paveikslų.

Ginamieji disertacijos teiginiai

1. Parinkus tinkamas sąlygas (reaguojančių medžiagų santykį, reakcijos trukmę ir temperatūrą) KCl ir NH₄H₂PO₄ mainų reakcijos būdu galima gauti kokybišką KDF (su nedideliu azoto ir chloro priemaišų kiekiu).
2. Naudojant mikroceliuliozę būgniniu granuliatoriumi galima sugranuliuoti konversijos būdu gautą KDF, taip pagerinant jo savybes (padidinant prekinės frakcijos kiekį ir stiprį, sumažinant higroskopiją).
3. Panaudojant konversijos metu susidariusius pokristalizacinius tirpalus galima pagaminti skystasias NPK trąšas, taip sukurti beatliekinę kalio dihidrofosfato gamybos technologiją.

IŠVADOS

1. Nustatyta, kad KCl ir NH₄H₂PO₄ sąveikos vandeniniuose tirpaluose produktas, kurio cheminė sudėtis (49,7 % P₂O₅, 38,1 % K₂O) ir K₂O: P₂O₅ santykis (0,67 m/m) geriausiai atitinka gryno KH₂PO₄ sudėtį (52,2 % P₂O₅, 34,6 % K₂O) ir santykį (0,66 m/m) gaunamas, kai reakcijos trukmė 5 val., temperatūra 60 ºC, reaguojančių medžiagų molinis santykis = 0,8:0,2.
2. Nustatyta, kad giauriausiau granuliuoto kalio dihidrofosfato rodikliai (65 % prekinės frakcijos, 8,7 N/gran. statinis stipris, 1,7 % drėgmės) gaunami, kristalinį kalio dihidrofosfatą granuliuojant būgniniu granuliatoriumi kai: žaliavų mišinyje yra 5 % celiuliozęs; 21 % drėgmės; temperatūra 55–65 ºC; granuliatoriaus sukimosi greitis – 27 aps/min.
3. Nustatyta, kad galima pagaminti skystąsias 4–5–15 markės trąšas, į po kalio dihidrofosfato kristalizacijos likusius tirpalus įdėjus 6 % CO(NH₂)₂ arba 8 % NH₄NO₃, kurių kristalizacijos temperatūra yra atitinkamai 15 °C arba 6 °C.


5. Nustatyta, kad skystosioms kompleksinėms trąšoms su amonio nitratu gaminti, saugoti ir vartoti netinka anglinis plienas (St3), nes jo korozijos gylio indeksas (6,81 mm/metus) yra didelis, tačiau gali būti naudojamas legiruotasis plienas (35S22099), nes jo korozija nevyko.

6. Apibendrinant gautus rezultatus, sukurta principinė technologinė schema ir parinkti pagrindiniai parametrai granuliotam kalio dihidrofosfatu (49,7 % P₂O₅; 38,08 % K₂O, 1,9 %N ir 1,9 % Cl) ir skystosioms kompleksinėms 4–5–15 markės trąšoms gaminti.