

Phosphorus pentoxide from Kazakhstan phosphorus as a base for production of polyphosphoric acids (PPA) in the cascade reactors system

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The polyphosphoric acids (PPA) were synthesized in a cascade reactors system from P_2O_5 obtained from the burning of Kazakh phosphorus. Presented system provides guidelines for the PPA production process using phosphoric acids only at concentrations above 100% (in conversion to H_3PO_4). Polyphosphoric acids are processed in a cascade reactors system, where the in 1st concentration of PPA is increased by addition of P_2O_5 , while in the 2nd reactor PPA is diluted with the use of 85% phosphoric acid. Produced PPA can be obtained in the 100–118% range and is characterized by high chemical purity due to the reduction of the corrosivity of the reaction, which results in very low content of iron (below 2 ppm Fe).

Keywords: phosphorus pentoxide, PPA, polyphosphoric acid, cascade reactors, kazakhstan phosphorus.

INTRODUCTION

Polyphosphoric acid (PPA) is widely used in the industry. It is used, inter alia, in chemical syntheses as a semi-finished product, as a catalysing and water binding agent in organic syntheses and as a modifier for asphalts^{1–3}.

Obtaining polyphosphoric acid in industry is most often carried out in the process of concentration of the phosphoric acid by an evaporation¹. The conditions of carrying out this process in a high temperature and strong corrosive properties of hot phosphoric acid, requires highly specialist materials resistant to the process environment^{1, 3}. Additionally, it is necessary to apply sources of heat that ensure high temperature that enable polycondensation of the acid^{4, 5}. In this article there have been presented possibilities and conditions for production of polyphosphoric acids with concentration up to 118% (in conversion to H_3PO_4) in cascade reactors system.

When executing the targeted project under name: “Developing highly innovative technology for obtaining polyphosphates based on a solid P_2O_5 ”, carried out—with a financial support from the European Union funds as a part of the POIG 1.4 Programme—in laboratory conditions and a semi-technical scale, there were examined possibilities for producing various concentration polyphosphoric acids with the use of 85% of thermal phosphoric acid and solid phosphorous pentoxide obtained from burning Kazakhstan phosphorous as raw materials⁶.

DESCRIPTION

The developed technology for obtaining a polyphosphoric acid is based on dosing an adequate quantity of a solid phosphorous pentoxide P_2O_5 to the PPA and subsequently diluting the obtained highly concentrated PPA to a desired concentration. Typical reaction between the solid P_2O_5 and diluted phosphoric acid, that contains water that is not bound chemically, is highly exoenergetic: $P_2O_5 + 3H_2O = 2H_3PO_4 + Q$

Carrying out a direct synthesis of polyphosphoric acid from phosphoric acid and phosphorous pentoxide is not favourable in the process-apparatus aspect due to impetuosity of reaction, system corrosiveness and a significant amount of the produced heat.

Due to application of the described method it is possible to obtain a polyphosphoric acid with a required concentration by diluting the initially obtained PPA with concentration of 116–118% (in conversion to H_3PO_4) with the 85% of phosphoric acid. Opposite to a direct reaction of the 85% of the phosphoric acid with P_2O_5 , the reaction between the 85% phosphoric acid and 116–118% of PPA is characterized by soft conditions of carrying out the process in the temperature range below 100°C. The reaction between $PPA \geq 100\%$ and solid P_2O_5 is characterized by a simpler process control.

The PPA obtaining process was divided into two stages carried out in two tank reactors (R1) and (R2) with a working capacity of 0.1 m³ each. The reactors are equipped with a heating-cooling jacket and mechanical stirrer. The entire system is thermostated with water from an insulated tank (V1) with working capacity of 1 m³.

The reaction of a solid P_2O_5 with $PPA \geq 100\%$ (in conversion to H_3PO_4), is carried out in the (R1) reactor where occurs a synthesis of a highly concentrated PPA ($\geq 116\%$). When the reaction is finished polyphosphoric acid is drained gravitationally to reactor (R2), where PPA is diluted by phosphoric acid to a desired concentration. The installation diagram is shown in Figure 1.

EXPERIMENTAL:

In order to initiate the discussed process it is necessary to dose into reactor (R2) a ready to use polyphosphoric acid with concentration $\geq 100\%$ (in conversion to H_3PO_4), in the minimum amount of 50 dm³. It is also possible to run a one-time synthesis of such PPA in (R2) in reaction between P_2O_5 and phosphoric acid (V).

As part of the carried out works, in the (R2) reactor polyphosphoric acid with concentration of 106% was produced in amount of approx. 70 dm³. Obtained polyacid was a base to start the process in the discussed manner.

With the use of a gear pump the polyphosphoric acid with concentration $\geq 100\%$ in the amount of 50–70 dm³ is pumped from reactor (R2) to the initial synthesis reactor (R1). Next, using the calculation table, an adequate amount of phosphorus pentoxide must be dosed into reactor (R1) to obtain an acid with concentration of 116–118% (in conversion to H_3PO_4). The process of

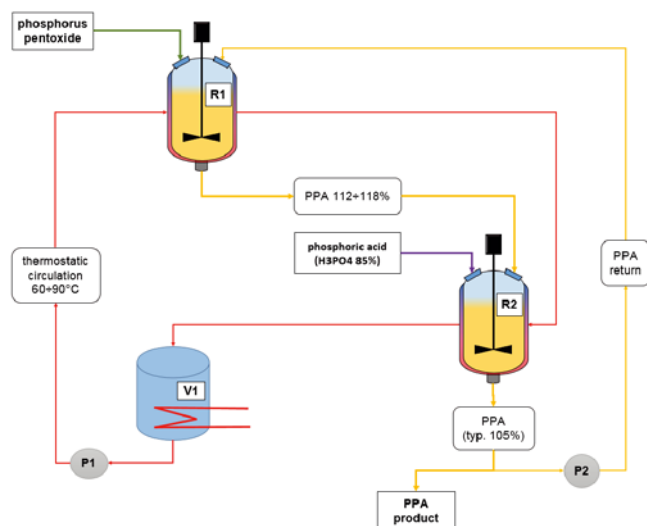


Figure 1. Experimental installation for the production of PPA in a cascade reactor system

dosing of P_2O_5 and reaction with a polyphosphoric acid lasts from 4 to 6 hours. As a result of the reaction there is produced heat that is carried away from the (R1) reactor with water jacket to the circulating water tank (V1). After the first reaction stage is finished, a lower discharge valve is opened in (R1). This causes outflow of the 116–118% polyphosphoric acid with the use of gravity from the initial synthesis reactor (R1) to the second reactor (R2). PPA collected in the reactor (R2) is then a subject to the process of diluting with the use of 85% H_3PO_4 , to the concentration as needed at that time. As part of the ongoing works, the main focus was to obtain the 105% PPA that is used as asphalts modifier^{7,8}. The polyphosphoric acid diluting reaction results in emitting extra quantities of heat carried away by the water jacket of the reactor (R2) and accumulated in the circulating water tank (V1). Proper circulation between the tank and reactors is ensured by a centrifugal pump (P1). The thermostatic circulation is common for both reactors (R1 and R2), which causes even distribution of the accumulated thermal energy in the whole process.

The ready to use 105% phosphoric acid is brought out from the reactor (R2) by gravity flow in two streams. The first one is the PPA 105% commercial product, whereas the other is returned to reactor (R1) through the gear pump (P2) as a semi-finished product and used to start the synthesis.

The discussed process allows for a work with PPA with concentration only above 100% (in conversion to H_3PO_4).

This is beneficial in field of maintaining a properly high polycondensation forms in the ready to use PPA. The chemical process is based on the phosphoric acid polycondensation effect that takes place after the 93% concentration of H_3PO_4 is exceeded¹. The polycondensation starts with creation of the $H_4P_2O_7$ pyrophosphoric group. With further increase of concentration, due to P_2O_5 addition, after exceeding 100% (in conversion to H_3PO_4) in the reaction mixture is no more free water, with which P_2O_5 would come into reaction. Due to this fact a significant polycondensation process acceleration takes place and creation of long PPA chains. On this stage of process a significant decrease of the emitted heat is observed. To ensure proper speed of reaction, heat from the circulating water tank (V1) was used. Heat energy buffered in the tank (V1) is sufficient to thermostate the experimental system in an optimum range of process temperatures from 50 to 90°C (depending on the maximum concentration of the polyphosphoric acid in the system). When the discussed process is ongoing, in the experimental system there were observed fluctuations of the circulating water temperature from 60°C on the stage, where the process was solely carried out in (R2), up to 90°C when reactions took place both in (R1) and (R2).

Due to high viscosity of PPA in low temperatures¹ if there is a necessity to store polyacid in reactor (R1) or (R2) in a liquid form and with the first start-up of the system there is a need for additional heating/thermostating of the circulating water in the minimum temperature of 60°C. Due to this, an additional source of heat in the form of a steam coil was installed in the tank (V1).

RESULTS

In the experimental system a few types of polyphosphoric acid were produced, products are characterized by high chemical purity and high content of highly condensed polyphosphoric groups. The content of metals was marked with the ICP-OES method using a standard curve for each of the determined elements, whereas the polyphosphoric forms composition analysis was carried out with the use of a gradient liquid chromatography. Chemical analysis results of the obtained polyphosphoric acid batches have been provided in the Table 1.

Determination of polycondensation forms in PPA can be done by carrying out an ion chromatography analysis. Determination of polyphosphates is carried out on an anion-exchange column (IonPac AS7), the eluent is

Table 1. Summary of chemical analyses of received PPA, polycondensation forms and impurities

Parameters	105 % H_3PO_4	111 % H_3PO_4	114 % H_3PO_4	117% H_3PO_4
P_2O_5 [%]	76.08	80.21	82.53	84.78
As [ppm]	42.3	35.8	37.0	24.9
F [ppm]	0.616	–	–	–
Hg [ppm]	0.01	0.01	0.01	0.01
Pb [ppm]	<0.2	<0.3	<0.2	<0.3
Cd [ppm]	0.048	0.114	0.125	0.08
Fe [ppm]	1.56	1.57	1.89	1.24
Density (at 80°C) [g/cm^3]	1.9	1.95	2.0	2.02
Ortho (PO_4) [%]	49.5	17.9	11.87	2.85
Pyro (P_2O_7) [%]	38.3	35.6	18.89	7.48
Tri (P_3O_{10}) [%]	10.0	23.4	17.79	9.65
Tetra (P_4O_{13}) [%]	1.8	12.4	14.59	10.65
Higher (P_n) [%]	0.4	10.7	36.85	69.37

a solution of 0.5M KCl and 3.2 mM EDTA. After the separation on the column, sample undergoes post-column derivatization based on the hydrolysis of polyphosphates in a dilute HNO₃ solution. Hydrolysis leads to the formation of simple orthophosphates which react with the molybdenum-vanadium reagent in the post-reaction loop creating a colored complex. This reaction is characteristic for orthophosphates group, obtained complex is determined with use of spectrophotometric UV-vis detector at a wavelength of 410 nm. Lower condensated acids are more mobile and their retention time is lower than it is in case of higher condensated forms. In Figure 2 there has been presented a chromatogram for PPA 117.2%. Orthophosphate forms have the shortest retention time with peak at 4.76 min (1). Another peak belongs to the pyrophosphate groups 6.54 min (2), whereas tripolyphosphate forms appear in the chromatogram at 15.30 min (3). Subsequent higher condensated forms of polyacid are present in the graph from minute 21 (4), wherein from minute 27 to 30 there can be observed a wide peak of the mixture of long chain forms of PPA.

SUMMARY

Due to application of a method for obtaining a polyphosphoric acid in the cascade reactors loop, there was avoided operation of the system in the temperature range disadvantageous for industrial the apparatus.

In the process the reaction between H₃PO₄ below 93% concentration and solid phosphorus pentoxide was eliminated, due to this the system corrosiveness was limited,

which allows that a classic acid-proof steel is used for the system construction (e.g. AISI 316L).

Due to avoidance of a turbulent course of reaction between P₂O₅ and phosphoric acid with low concentration, the issues with carrying away heat of reaction and boiling in the system was eliminated, which facilitates control over the production process.

LITERATURE CITED

1. Gilmour, R., *Phosphoric Acid. Purification, Uses, Technology and Economics*, CRC Press, Boca Raton, 2014, 183–201.
2. Jaroszek, H., *Kwas polifosforowy w modyfikacji asfaltów drogowych*, CHEMIK 2012, 66, 12, 1340–1345.
3. Cichy, B., Machej, J., Krystek, A., Kalinowski, Z., Jamroz, A. & Ratka, G., Polish patent, PL 177354, November 30, 1999.
4. White, A.G. & Smith, T.E., Work L.C., US patent, US 3656897, April 18, 1972.
5. Kopyleva, B. & Shvartsman, Y., US patent, US 5824132, October 20, 1998.
6. Urbańczyk, L., Milde, D., Figura, M., Cholewa, J., Kurzańska, A., Ochman, M., Milde, A. & Piś, W., *Przem. Chem.* 2018, 97, No. 4, 557. DOI: 10.15.15199/62.2018.4.8.
7. Baldino, N., Gabriele, D., Lupi, F.R., Rossi, C.O., Caputo, P. & Falvo T., *Rheological effect on bitumen of polyphosphoric acid (PPA) addition*, *Construction and Building Materials*, Vol. 40, March 2013, 397–404.
8. Masson, J.F., *Brief review of the chemistry of polyphosphoric acid (PPA) and bitumen*, *Energy & Fuels*, Vol. 22, No. 4, June 2008, 2637–2640.

No.	Time min	Peak Name	Area mAU*min	Rel.Area %	Amount ppm	Rel.Amount %
1	4.76	ortho	17,947	3.76	37,6947	3,76
2	6.54	pyro	45,892	9.63	96,3910	9,63
3	15,30	tri	55,773	11.70	117,1449	11,70
4	24,73	higher	357,094	74.91	750,0319	74,91
TOTAL:				100.00	1001,26	100,00

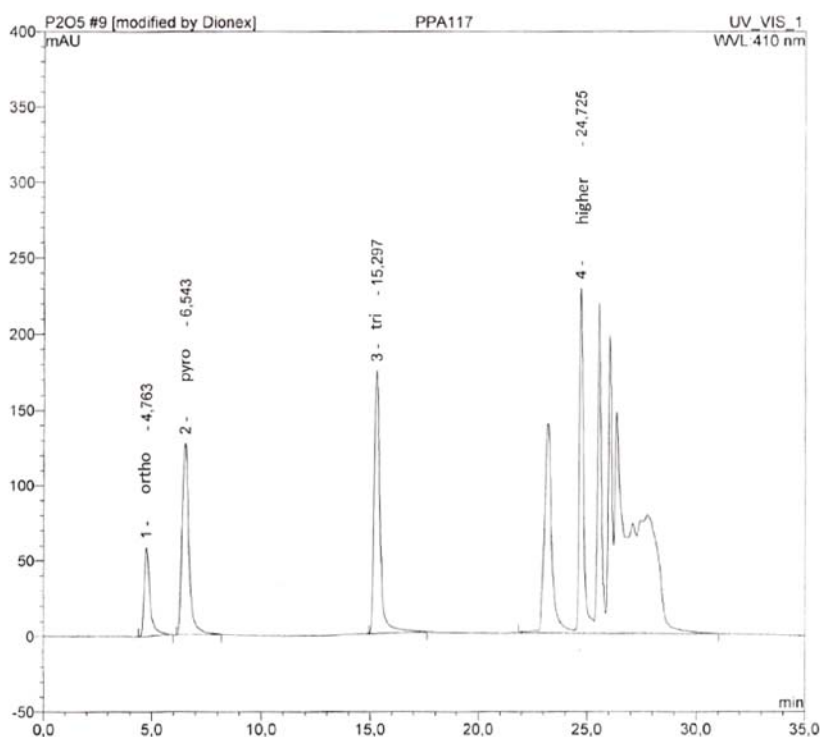


Figure 2. Results of chromatographic analysis of PPA 117.2%