STUDY OF THE KINETICS OF THE GLYPHOSATE SYNTHESIS REACTION BASED ON INORGANIC AND ORGANIC COMPOUNDS

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ABSTRACT

The strategy for sustainable development of the agricultural sector of the agricultural economy, in particular, requires improvement in agriculture and the need to optimize the use of mineral fertilizers and pesticides. Without improvement and application of reliable specialized methods of pest control, weeds and diseases of agricultural crops, the loss of grain and vegetable products can reach up to 25-30%. At the same time, the agricultural sector has been undergoing some changes associated with the transition to resource-saving technologies, tillage and application of crop protection agents, etc. Analysis of tendencies of production and application of pesticides was carried out according to the annual reports of the Ministry of agriculture of Kazakhstan and data of the Committee of ecology and nature management of the Republic of Kazakhstan. Glyphosate as one of the representatives of fungicides and pesticides is also used in the treatment of tree trunks and row spacing in gardens and vineyards. Reliable destruction of perennial weeds that can be removed only in a few treatments during row-to-row cultivation. Make the problem of application and as desiccants relevant. As a positive effect, it is indicated to reduce the infestation of fields with perennial weeds and sometimes with annual ones, sown areas and sunflower, peas, soybeans, rapeseed, and corn, counteracting the formation and maturation of weed seeds. It should be noted that weeds should be in the active phase of vegetative growth, since otherwise the result may not be effective.

Key words: kinetics, synthesis, phosphoric production, organic compound, glyphosate, physical and chemical properties

INTRODUCTION

The use of glyphosates can be characterized by two periods. The first is the autumn eradication method, which destroys root and rhizomatous weeds, and the second when processing the soil with glyphosate. In these cases, glyphosate is used in the initial period of culture shoots to destroy any weeds-one-two-and perennial, also wintering. The advantages of using glyphosate are that, without having a harmful effect on the soil, they destroy all vegetation before the crop sprouts. Therefore, the most active forms of glyphosates based on ammonium compounds are used in smaller (almost 30%) doses-2-3 l. this was the main purpose of using the reture of ammophos and phosphorus slime in the preparation of glyphosate [1, 2].

In accordance with the composition or preparations contain at least two herbicides and one surfactant. The first component of the compositions may be, N-phosphonomethyl-glycine (glyphosate), its salt or adduct, or a compound that is converted to glyphosate in plant tissues or a glyphosate ion. It should be noted that the term "glyphosate" provides for the coverage of many derivatives that do not require a different interpretation. Salt glyphosate, applied in accordance include salts with alkaline metals such as sodium and potassium salts, ammonium salts, alkylammonium salts such as C1-16 alkylammonium or alternative C3-16 alkylammonium, diammonium salt, dimethylammonium, alkylamine salt, in the form dimethylamine and Isopropylamine salts, alkanolamine salts (e.g., C1-16 alkanolamine or alternative C3-16 alkanolamine, for example, ethanolamine salt), alkylsulfonate salts (e.g., C1-16 alkylsulfonate, for example, trimethylsulfonium salt), sulfoxonium salts or mixtures or combinations thereof. Herbicidal properties of N-phosphonomethyl-glycine and its derivatives were first discovered by Franz, and then disclosed and patented in the works [3].

Various N-phosphonomethylglycine salts are commercially significant, due to the fact that they are highly soluble in water. Most of the salts listed in the work are very well soluble in water form highly concentrated solutions and can be used by diluting them at the site of their application. In accordance with the relevant glyphosate herbicide, a solution containing a herbicide -effective amount of glyphosate and other components can be used in the treatment of plant foliage. Heterocycle groups include heteroaromatic groups such as furyl, thienyl, pyridyl, oxazolyl, pyrrolyl, indolyl, quinolinyl or isoquinolinyl, etc., and non- aromatic heterocycles such as tetrahydrofuryl, Tetra-hydrothyenyl, piperidinyl, pyrrolidino, etc. Substitutes containing one or more of the following groups: hydrocarbyl, substituted hydrocarbyl, keto, hydroxy, protected hydroxy, acyl, acyloxy, alkoxy, alkenoxy, alkynoxy, aryloxy, halogen, amido, amino, nitro, cyano, thiol, complex thioester, simple thioester, ketal, acetal, ester or simple ester.

The research was carried out on an enlarged laboratory facility in two stages [4].

At the first stage, phosphorous acid and phosphoric acid were obtained from yellow phosphorus. phosphorous anhydrite was obtained in the form of a white flake-like material by burning it at a low-temperature oxidation plant in the temperature range of 200-320 °C, the optimal temperature is 250-200 °C, and insufficient oxygen oxidation of dry air [5]. The resulting phosphorus trioxide powder was dissolved in water to form an acid by reaction

$$P_4O_6+H_2O=4H_3PO_3$$

Phosphoric acid was obtained from phosphorus in the phosphorus combustion and hydration unit at the Zhambyl branch of «Kazphosphate» LLP (Novo-Zhambyl phosphorus plant). The resulting acids were then used in the synthesis of glyphosate at the plant, in reactors equipped with mixing devices and jackets to maintain the temperature with hot water in the reaction zone at «Axeminvestcompany» LLP, Taraz. When, receiving glyphosate are given in the acts of experimental tests (Fig. 1).

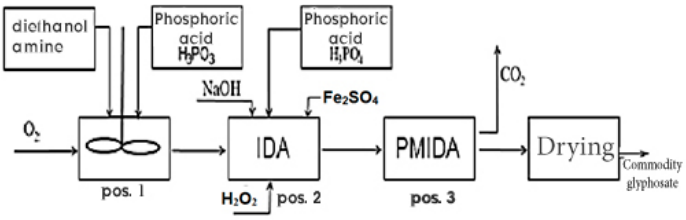


Fig. 1. Schematic diagram of obtaining glyphosate

MATERIALS AND METHODS

According to the proposed technology, diethanolamine and phosphorous acid obtained from phosphorus and phosphoric acid are used as starting materials for the synthesis of the imnodiacytonitr sodium salt. At the second stage of the process, where sodium alkali and iron sulfate is used as catalysts, and hydrogen peroxide is used as a reagent for the oxidation-reduction process [6].

After their mixing, the (IDA) is synthesized, which is exposed to phosphoric acid, in the second stage, also obtained from the phosphorus of the phosphoric sludge.

RESULTS AND DISCUSSION

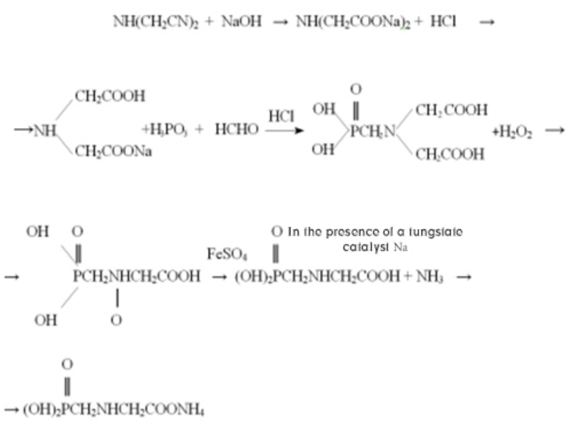
The preparation of glyphosate can be represented as a first -stage reaction:

$$(CH_2CH_2OH)_2NH+H_3PO_3+1,75O_2 \rightarrow (CH_3COCH_3)_2NH+H_3PO_4+CO_2, \qquad (1)$$

and in the second stage , the reaction takes place:

$$(CH_3COCH_3)_2NH+H_3PO_4+NaOH+4,5O_2 \rightarrow C_3H_8NO_5P\downarrow+3CO_2\uparrow+4H_2O+NaOH \qquad (2)$$

The process of glyphosate synthesis, with the formation of a strictly targeted product, can be represented as the following total reaction:



The resulting precipitate of phosphate methylated amino acids is subjected to recovery of glyphosate by oxidation with use of hydrogen peroxide.

Iminodiacetonitrile, reacting with an aqueous solution of sodium hydroxide and hydrochloric acid, forms ammonia and sodium iminodiacetate, which, interacting with an aqueous solution of phosphorus trichloride and formaldehyde, passes into PMIDA.

The resulting product is concentrated, subjected to membrane separation until a 10-20% aqueous solution of glyphosate is formed, and treated with ammonia gas, with further production of ammonium glyphosate [7, 8, 9].

During this total reaction, ammonia, water, and sodium chloride are formed.

Phosphorus trichloride is necessary for the production of H3PO3 -phosphorous acid, used at the stage of PMIDA synthesis in the presence of formaldehyde, which is also formed in the process of oxidation- reduction of PMIDA by hydrogen peroxide in the presence of sodium tungstate and iron sulfate, which shift the reaction to the right side of the chemical equilibrium. Therefore, this stage can be eliminated by using phosphorous acid in industrial conditions [10, 11].

Thermodynamic calculation of the above reactions 1 and 2 showed that it is possible when a certain amount of heat is introduced from the outside.

To obtain phosphorus pentoxide, liquid yellow phosphorus was burned in the air oxygen stream at an oxygen excess coefficient of about 1.2-1, 3 and combustion temperatures of 650-700oC.

The P_2O_5 obtained during the oxidation process was directed to the so-called hydration stage, by absorbing phosphoric anhydrite with water and passing P_2O_5 through the water layer from the bottom up, at a ratio of P_2O_5: water 1:3.3, it converts≈ 73% H_3PO_4 to orthophosphoric acid, i.e. 1.0-1.1 kg / hour of phosphorus 5, 0-6, 5 kg / hour of water.

According to the developed technological scheme shown in Fig. 13, diethanolamine and formaldehyde were fed in certain ratios to the reactor pos. 1, where the temperature was maintained in the range of 60-80 °C, in order to reduce the viscosity of the reagents used and increase their reactivity.

Then to the reactor pos. 1 introduces phosphoric acid obtained from phosphorus contained in the phosphoric slag, and stir until a homogeneous mixture is obtained, in the presence of hydrochloric acid. From the reactor pos. 1 the resulting iminodiacetonitrile is poured into an enameled reactor pos. 2 where phosphoric acid, also obtained from phosphoric sludge, is fed.

The pos. 2 reactor is fed sodium alkali and iron sulfate, which play the role of a catalyst, to accelerate the reaction.

Iminodiacetonitrile, reacting with an aqueous solution of sodium hydroxide, hydrochloric acid and formaldehyde, passes into PMIDA- phosphoromethyl-iminodiacetonitrile.

Then, for the redox reaction, hydrogen peroxide is also fed to the reactor pos. 3 to convert iminodiacetonitrile in the presence of formaldehyde to phosphoromethyl-iminodiacetonitrile.

Ammonia, carbon dioxide, water, sodium chloride, and glyphosate obtained during the redox reaction are concentrated, fixed, and the resulting white flake-like precipitate, after drying at 150-200 °C, passes into a white crystalline glyphosate.

In addition, experiments were also conducted to study the degree of incomplete oxidation of the lower phosphorus oxides P_4O_6 and P_4O_{10} from the temperature in the presence of dry air oxygen in order to determine the highest yield of phosphorous and phosphoric acids shown in Fig. 14.

Studies to determine the degree of phosphorus oxidation were performed on the unit shown in Fig. 15. The analysis of products was performed in the laboratory of "Axseminvestcompany "LLP. In the process of vacuum evaporation of the resulting solution, hydrogen chloride evaporates and leaves colorless hygroscopic crystals of phosphoric acid that are difficult to oxidize in air, which can be used to produce glyphosate using the developed technology [12].

During the tests, the possibility of synthesizing glyphosate was established. Data of spectral analysis of the Regional testing laboratory of engineering profile of M. Auezov SKSU definition of its main components is shown in Fig. 2 and 3.

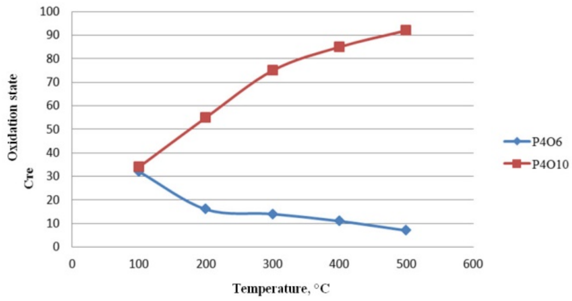


Fig.2. The degree of incomplete oxidation of the lower oxides of dry phosphorus by air oxygen from the temperature

In the course of determining the optimal parameters of the glyphosate production process from the temperature and contact time of inorganic and organic compounds, it was found that the optimal temperature for conducting the redox process ranges from 125-140 °C, and the contact time is about 180-240 minutes, at which the product yield is from 65 to 87% [13].

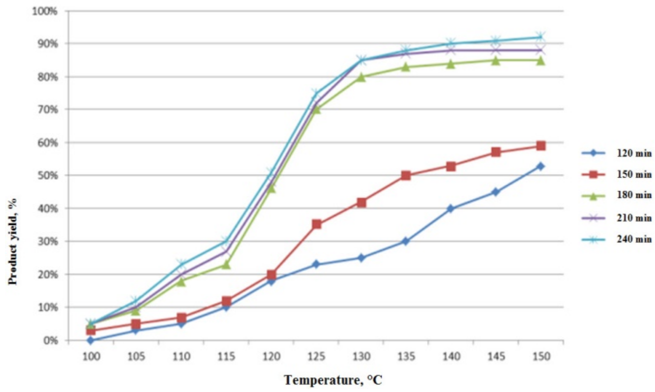


Fig.3. Dependence of glyphosate yield on process temperature and time

CONCLUSION

Thermodynamic calculation of the possibility of reactions of interaction of inorganic and organic compounds based on phosphorous and phosphoric acids with diethanolamine and iminodiacetylnitrile in the presence of catalysts-sodium alkali and iron sulfide .

The possibility of these reactions occurring without introducing heat from the outside has been established. However, to maintain the process temperature in the reactors, it is necessary to maintain the temperature in the reactor jacket within 125-1400C. Studies have been conducted to determine the oxidation of lower phosphorus oxides P_4O_6 и P_4O_{10} in the presence of dry air oxygen at temperatures from 100 to 5000C. It was found that with increasing temperature, the oxidation state of P_4O_{10} increases, and P_4O_6 on the contrary decreases from more than 30% to 3000C by 75 and 15%, respectively. They are necessary in the process of producing glyphosate at the first and second stages in the formation of phosphorus trichloride and phospho-formethylamic acids in the presence of hydrogen peroxide.

The chemistry is justified and the kinetics of the reaction of glyphosate synthesis based on inorganic and organic compounds in the presence of hydrochloric acid and hydrogen peroxide, as well as catalysts, is studied.

The optimal time of 180-240 minutes and the process temperature in the range of 125-1400 C at which the product yield is from 65 to 87% are set.

Product was analyzed using a scanning electron microscope JSM 6390 LV (Japan) obtained at various optimal temperatures during the process.

It was found that depending on the parameters of the process, the composition of glyphosate has minor differences in the content of phosphorus from 13.85 to 14.29; chlorine about 1.7; nitrogen in the range from 14.25 to 14.74; sulfur about 0.65 and carbon from 27.9 to 28.9%.

A technological scheme for producing glyphosate has been developed that includes the stages of displacement, conversion of a reaction mixture consisting of diethanolamine and phosphorous acid into iminodiacetonitrile, when exposed to phosphoric acid , in the presence of catalysts of sodium alkali and iron sulfide , it is possible to obtain phosphor- methylated amino acids, which after drying passes into glyphosate [14].

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