

Research of the Mechanism Oxidation of the Phenol by the Electrical Spark-Over in the Liquids

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Abstract – This paper studies the reaction development mechanism in phenol water solutions at the moment of electric pulse breakdown in the air-isolated system.

Phenol is one of hazardous by-products contained in the effluent of chemical and woodworking industries and in stagnant waters. Purification of water from phenol is carried out through its oxidation by strong oxidizing agents. Lately, numerous works describing phenol oxidation in phenol water solution by oxidizing agents which are initiated by different types of discharges formed in or above the solution have appeared. Practical application of the method is prevented by the fact that the mechanism of this process is not enough studied.

It is known [1], that during the development of discharge canal primary electrons are generated in the liquid in the area of anode and positively charged canal head. Liquid is ionized. In case when water is used as a liquid, basing on energy release in the canal it is assumed that canal plasma substance contains H^+ ions, OH^- ions, etc., which are allowed for when studying substance conductivity in primary canal.

The influence of ionizing particle on water in respect to chemical processes initiation in it is well studied.

According to [2], at the first stage of ionizing particle influence on water by the moment of time 10^{-6} s excited H_2O^* , super-excited H_2O^{**} water molecules, H_2O^+ ions, and excited secondary electrons are generated. Electrons loose their energy up to the level of medium condition for 10^{-15} s. At the same time under-excited electrons (energy is less than 7.4 eV) appear. Physical-chemical stage starts approximately at 10^{-14} s. Thermal equilibrium is established in the system. For this period of time dissociation of excited and super-excited molecules, autoionization of super-excited molecules and ion-molecular reaction of $H_2\dot{O}^*$ with H_2O occurs. Singlet excited molecules of water (excitation energy of 8.4 eV) decompose into H and OH. In $H_2O^* + H_2O \rightarrow H_3O^+ + OH$ reaction radical and dry ion H_3O^+ appear. The probability of oxygen atom generation during water molecule decomposition is insignificant (excitation energy of 0.17 eV) and its occurrence is disregarded.

Under excited electrons loose their excess energy for 10^{-13} s and become thermo isolated. Such quasi-free electrons and probably the electrons with excess kinetic energy may react with solutes in concentrated

solutions; they are called dry. Electrons may partially hydrate even before the complete loss of excess energy. The time of electrons hydration at room temperature is $4 \cdot 10^{-13}$ s.

Thus, by the end of physical-chemical stage \bar{e}_{ag} , H, OH, H^+_{ag} , and H_2 exist in water; OH and peroxides possess oxidizing properties, \bar{e}_{ag} , and hydrogen have reducing abilities. On a chemical stage the mentioned particles diffuse from their generation area and react with each other and with other solutes. The reaction start depends on the concentration of a solute and its reactivity. The activity of hydroxyl is higher than that of hydrogen and oxidizing processes develop in the first place. Reducing reactions become possible after hydroxyls fixation by acceptors. In case with diluted solutions (10^{-3} – 10^{-4} mole/l) reactions begin at 10^{-12} time order. At first, the particles of ionized water react with each other, then by 10^{-7} s their reaction with solutes become noticeable. For concentrated solutes, as it has already been stated, the reactions with dry holes of H_2O^* and with dry electrons for 10^{-13} – 10^{-12} s are possible.

Basing on this, we have analysed the results obtained under the influence of electric pulse breakdown on phenol water solute.

Pulse current generator (voltage amplitude up to 70 kV and variable capacity of capacitor bank of 0.1–0.4 μF) was used as a pulse voltage supply. Cylindrical work chamber was made of polyethylene, in-built system of electrodes of “point tip to flat tip” structure – of stainless steel. The chamber was supplied with gas-collecting tube with backflow condenser for collecting gas products. The chamber was also equipped with a built-in temperature control device for maintaining a given temperature level. Phenol concentration was changed from 1 to 5 g/l. Gas products were analysed chromatographically. The concentration of phenol and its destruction products was determined photometrically and by way of bromide-bromate titration. The concentration of carboxylic acids was determined using volume titration method; besides pH was controlled. Hard products were filtered.

In the course of work it was found out that electric breakdown of phenol solute in water as well as electric breakdown of other liquids is accompanied by the process of gas generation. There is an induction period which lasts for 100–500 pulses depending on the energy of a single pulse during which gas is not evolved. Under the conditions when interelectrode space is 7 mm,

pulse amplitude is 50 kV, and the capacity of capacitor bank equals 0.2 mF, after having applied 3 hundred pulses over one litre of gas is evolved for the treatment of phenol solute with 2 g/l concentration, this is almost 10 times more than in case with distilled water. This effect is similar to the effect produced under the influence of ionizing radiation when loading organic substances into the water leads to a considerable increase in gas generation [2]. The more the number of pulses applied for system treatment, the higher the speed of gas generation is: it increases 30% upon application of 15000 pulses. This indicates the changes in the condition of the system being treated causing changes in discharge canal formation conditions in it.

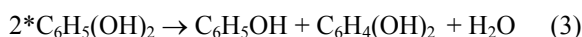
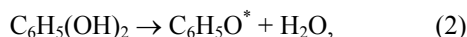
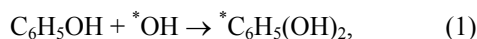
Table 1 gives the composition of gas products in two test samples of 210 and 1460 ml volume. The first sample hydrogen content is 98%. Its water content is 0.98%. The rest falls to CO, CO₂ and carbohydrates – methane, ethane, and acetylene. In the second gas sample hydrogen outlet decreases, oxygen outlet increases to 52%. Gaseous phenol oxidation products contain mainly CO – over 6%, CO₂ outlet is almost 6 times less. Methane, ethane, and acetylene persist in gas products over the experiment duration.

Table 1. Gas composition in step by step selected samples under breakdown of phenol water solute (2 g/l) by pulses with energy of 125 J

№	Gas sample volume (ml)	Hydrogen volume %	Oxygen volume %	Carbon oxide volume %	Carbon dioxide volume %	Methane volume %	Ethane volume %
1	210	98.65	0.98	0.35	0.18	0.03	0.002
2	1460	40.00	52.50	6.30	0.90	0.12	0.180

In our opinion, the first gas sample corresponds to the period when the process of excited water molecules decomposition into I and II is developing. The probability of oxygen atom occurrence is insignificant and it is not present in the sample. As the condition of the system changes oxidizing processes prevail and oxygen as a reaction product reaches the samples. That is why the composition of step by step selected gas samples during the experiment varies.

It is known from publications, that [3] radiolytic decomposition of phenol is mainly initiated by its reaction with *OH radicals:



through intermediate products to CO₂ and H₂O. Under the conditions of our experiment, when the system isolated from air is used, CO is generated instead of the expected CO₂.

Phenol solute changes its color and type under the influence of electric discharges: from colorless clear

solute to cream-colored suspension, and then changes to black. After sediment separation the solute turns into blue-green color tone in transmitted light which under longer treatment changes into dark brownish black

As it can be concluded from the above results, phenol concentration in solute treated by electric discharge decreases 70% after application of 6000 pulses with single pulse energy 250 J. Downtrend in phenol destruction speed is observed as the number of pulses applied increases.

Bromide-bromate titration gives higher estimates of phenol concentration in the solute than photometry, which indicates the presence of intermediate phenol oxidation products with double bonds binding bromine.

At the same time it should be noted that we have established after-effect: phenol concentration in the solute treated by electric discharges continues to decrease for more than 24 hours after treatment, and the more pulses were applied for solute treatment the more intensive this decrease is. The same effect is observed in case with water as well. Concentration of phenol in the solute prepared in water pretreated by electric discharges was decreasing for 24 hours and the more pulses were applied for its pretreatment the more intensive decrease is. This indicates that the reactions are developed in chain-like mechanism similar to the processes occurring in water and in water solutes under the influence of ionizing radiation.

The occurrence of mucon acid in addition to quinines from among intermediate products of phenol destructed in chain-like radical mechanism when treating solute by electric pulse discharges is registered. The occurrence of organic acids was established in our experiment as well. This is supported by pH solute decrease from 6.75 for phenol solute with concentration of 1.5 g/l to 4.5 after application of 6000 pulses with single pulse energy of 250 J. The types of acids formed under the studied conditions have not been identified.

The development of polymerization reactions of soluble products appearing when phenol is oxidized under the conditions of the experiment has been established. Soluble products were separated using salting-out method by the influence of KCl. Changing the concentration of KCl added step by step to phenol solute treated by 2500 pulses with energy of 250 J from 0.1 to 2.0 n with 0.1 step interval 19 independent phases have been identified. Example is in Fig. 1. Some of them exhibit tautomerism, that is they have benzenoid-quinoid structure. Some change their color from lilac to brown when pH changes from 4.5 to acid direction and from lilac to red-brown when pH changes from 8.0 to alkaline direction, preserving lilac color within the range of pH from 4.5 to 8.0, others – deepen yellow color when solutes are alkalinized.

Some products of phenol oxidation precipitate even at the stage of solute treatment by electric pulse discharges. Some of the particles are quite big in size and solid phase easily precipitate on a paper filter in the

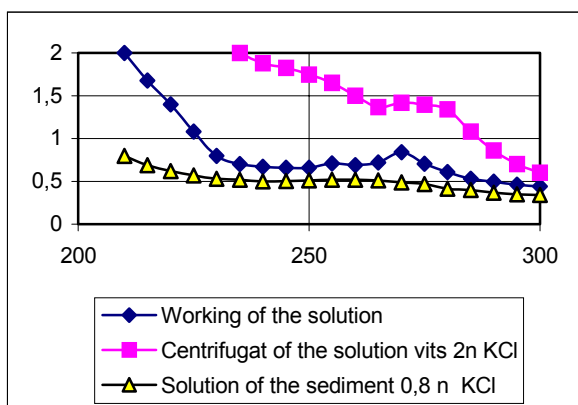


Fig. 1. Ultra-violet spectrum

form of a black tarry substance. The sediment is partially dissolved into alkali forming yellow solute. Transformed into solute compounds possess tautomeric properties: they are capable of color intensification from light-yellow to yellow when pH is changed from

4.5–5.5 in both acid and alkali directions. The product does not precipitate reversibly under the influence of acid. The sediment remained on filter turned into cream color similar to the color of suspension of the first stage of treatment of phenol solute by electric discharges. This product is not identified yet.

Thus, the application of electric pulse discharges in technologies of water and effluent purification from organic admixtures needs to be controlled in terms of the release of gas, soluble and solid products.

References

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