"Green" Technology for Nitric Acid Production: Is it Real?

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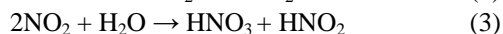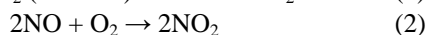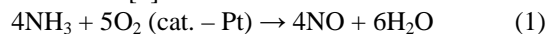E-mail: deadweasel@mail.ru, dejiijagbuji@yahoo.com

Abstract − This paper is intended to solve the problem of creating environmentally friendly technology for the nitric acid production. On the basis of existing production the analysis of produced waste and methods of disposal was carry out. The new technological solutions for the chemical industry that will achieve a low or non-waste technology is a cavitation of HOOH. Thus, due to the intensification of the absorption step, it is possible to increase the yield of the final product (HNO_3) by 20 % and reduce emissions of gaseous wastes to levels appropriate sanitary norm without further purification. In our opinion, this technological approach can be quite useful for the present chemical industry which completely rules out the catalytic-purification stage.

Key words − nitric acid, chemical industry, absorption, waste gases, waste materials, intensification, nitrogen oxides, hydroxyl radicals, ecologically pure technology.

I. Introduction

In modern time nitric acid, undoubtedly, is the 2nd largest most widely produced inorganic compounds, which is also utilized as a raw material for inorganic synthesis in the chemical industry to produce fertilizers and explosive [1]. The production of nitric-acid involves large-tonnage technology, also employs highly toxic compounds (NH_3 and NO_x) and that's poses an hazardous effect on the environment. Therefore an effective management and modernization of nitric acid production is one of the most important theoretical and practical problems faced by chemical engineers.

Currently, all nitric acid industry production methods are based on the catalytic oxidation of synthetic ammonia using platinum-rhodium catalyst (Oswald process). The reaction product of ammonia oxidation – nitrogen monoxide NO is further oxidized to nitrogen dioxide NO_2 (it should be noted, that the process occurs spontaneously and it intensification cannot be carry out). The resulting gases (a mixture of nitrogen oxides) undergo absorption by water. The production can be represented by following chemical reactions [2]:

$$4NH_3 + 5O_2 \text{ (cat. – Pt)} \rightarrow 4NO + 6H_2O \qquad (1)$$
$$2NO + O_2 \rightarrow 2NO_2 \qquad (2)$$
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \qquad (3)$$

After analyses of all these processes it is investigated that the waste materials and gases inevitably are generated in great quantity, and to demonstrate the results we designed a flow-scheme that shows all the paths of wastes produced during nitric acid production (see Fig.1). Fig. 1 shows the "Raw materials" which include compounds such as NH_3, O_2, N_2 (inert), water (with varying degree of purity), catalysts (Pt-Rh - for ammonia oxidation, Al_2O_3-V_2O_5 - for catalytic purification), CH_4 - for heating flows.
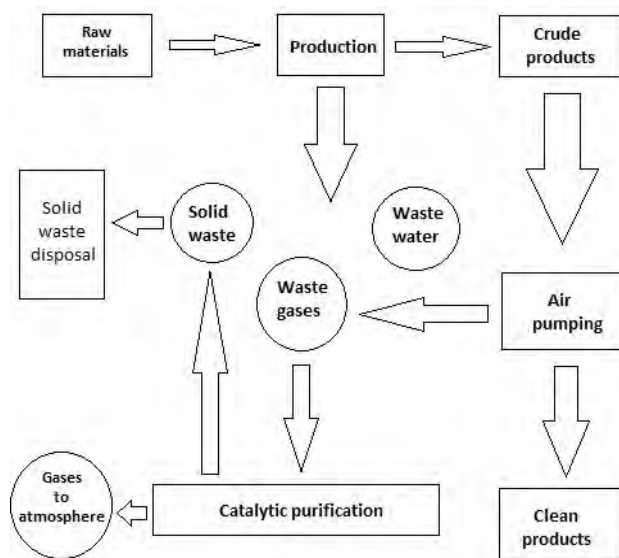

Fig. 1. Producing paths of waste and products
in nitric acid technology

After acid formation process (Eq 1-3) we have two different flows. The first flow-path is the crude products - they undergo the air pumping process because it is necessary to separate NO_x gases from HNO_3. Clean products are stored in the warehouse to be sold. Extracted nitrogen oxides mixed with another's waste gases. The second flow-path include three types of waste materials. Waste gases contains: NH_3, NO_x, N_2O, CH_4, CO_2, H_2O. The nitrogen oxides undergo catalytic purification. In present time, the chemical-industries use a large-amount of catalysts ($Pt > MnO_2 > V_2O_5 > CuO > Fe_2O$) [3]. In our case the plant use a catalytic-mixture Al_2O_3-V_2O_5 [4]. The solid-wastes obtained from nitric acid production needs to be deactivated or taken-away from the flows. Water after condensation (can contain NH_3, NO_x and some amount of HNO_3) while the steam with waste-gases flow forms the waste water.

II. Waste Gases

Waste gases constitute massive waste at the nitric acid plants. They are formed as a result of the nitrogen-dioxide absorption process (Eq.3), unreacted ammonia, production of burning methane and unreacted CH_4 and unreacted gas-reluctant (CH_4 or NH_3) after catalytic purification. In our opinion, the most difficult problem is the purification from NO_x. Therefore, we decided to look carefully at the absorption process so as to intensify the conventional method, and develop a low or non-waste technology [5].

In recent years, a large number of scientists have been inclined to think that the reaction of nitrogen dioxide with water occurs via the N_2O_4 dimer. In studies [2], it has been explicitly demonstrated that NO_2 does not directly participate in the reaction with water, but only subjects its dimer (N_2O_4) to hydrolysis. Under normal conditions, NO_2 exists in equilibrium with its dimer, dinitrogen tetroxide (N_2O_4) ($\Delta H_{dim} = -57.3$ kJ/mol). Composition of the mixture $NO_2 \leftrightarrow N_2O_4$ depends on the temperature and

pressure. With increasing temperature, the equilibrium shifts to favor nitrogen dioxide, while the liquefied N_2O_4 turns brown. By increasing the pressure at constant temperature, the degree of N_2O_4 dissociation decreases almost completely dissociated at 140° C [1].

Recently, studies by Finlayson-Pitts et al. [6] was first suggested that the absorption of NO_2 with water undergoes prior dimerization of •NO_2 radicals to form asymmetric dimer ONO–NO_2 with the highest dipole moment, which is shown in Eq. (4):

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2 \quad (4)$$

The structure of the transitions state of Eq. (4) calculated by the Density functional theory (DFT) method is shown in Fig. 2. Quantum chemical calculations have revealed that the asymmetrical structure with the trans-isomer configuration (see Fig. 2) has the highest dipole moment ($\mu = 2.6$ D).
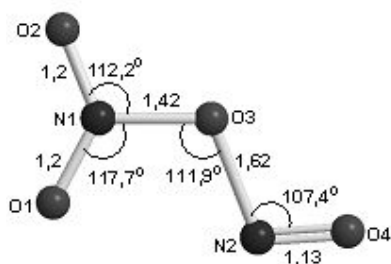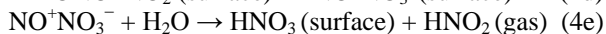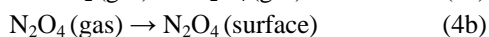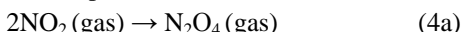

Fig. 2. Trans-isomer configuration of ONO–NO_2. Bond lengths are in Armstrong (Å). N_2O_4 is considered important surface specie in the reaction

According to the authors [6], the formation of asymmetric dinitrogen tetroxide ONO-NO_2 occurs on the surface of a thin film of water (a process we refer to as *the surface mechanism*). In the presence of highly polar water molecules ($\mu \approx 1,8$ D) is auto-ionization of dinitrogen tetroxide to form nitrate nitrozonium $NO^+NO_3^-$, which is a key intermediate in the process of nitric acid [7]:

$$2NO_2 \,(gas) \rightarrow N_2O_4 \,(gas) \quad (4a)$$
$$N_2O_4 \,(gas) \rightarrow N_2O_4 \,(surface) \quad (4b)$$
$$N_2O_4 \,(surface) \rightarrow ONO–NO_2 \,(surface) \quad (4c)$$
$$ONO–NO_2 \,(surface) \rightarrow NO^+NO_3^- \,(surface) \quad (4d)$$
$$NO^+NO_3^- + H_2O \rightarrow HNO_3 \,(surface) + HNO_2 \,(gas) \quad (4e)$$

We calculated, by the DFT energy profiles (Eq. 4) in the gas phase, without dimerization of NO_2 and prior dimerization of NO_2, as well as the process of acid formation in the presence of water molecules. To simulate the process of *the surface mechanism*, we calculated aqua-complexes reactants and reaction products of acid formation water clusters $(H_2O)_m$, with m = 2 – 4:

$$NO_2(H_2O)_2 + NO_2(H_2O)_2 \rightarrow NO^+NO_3^-(H_2O)_4 \rightarrow$$
$$HNO_3(H_2O)_3HNO_2 \quad (4f)$$
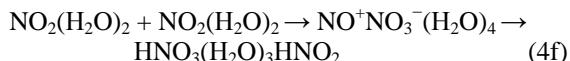
From the quantum chemical calculations, acid formation without the prior NO_2 dimerization has a higher activation energy (E_a=130.8 kJ/mol) than the reaction proceeding through prior formation of the asymmetric trans-isomer ONO–NO_2 (E_a= 80.1 kJ/mol). Therefore, one of the main requirements imposed on the absorption equipment in the production of nitric acid - the creation of a highly developed surface absorption, from our point of view, would be deemed a technological boom, confirming the mechanism [6], the mechanism of acid formation. The presence of thin films of water in the absorption column is realized by establishing a large number of plates as quantity of absorbed nitrogen oxides depends on the contact surface between gas and liquid.

Based on the above, it follows that the modernization of this stage production of nitric acid should be carried out in several directions. Firstly, in order to absorb nitrogen dioxides more actively, the absorption process has to be intensified, and secondly, to speed up the oxidation of NO to NO_2.

From our point of view, the modernization process of acid formation HNO_3 should be seen not only through the optimization of liquid-phase absorption of NO_2, but also through the possibility of acid formation in the gas phase. After the second product (Eq.3) - the nitrous acid is formed only in the gas phase and immediately decomposes to water and nitrogen monoxide NO.

Intensification of nitric acid formation. To deal with NO_x and disapprove of the catalytic cleaning of gases, we present a new method for the intensification of nitric-acid formation [5, 8].

In contrast to the absorption stage, where the hydrolysis of NO_2 occurs via surface mechanism on a thin film of water, we present nitric acid formation process entirely through the gas-phase by the interaction of nitrogen oxides with hydroxyl radical (•OH) and hydroperoxyl radical (•OOH):

$$NO + •OOH + M \rightarrow HNO_3 + M^* \quad (5)$$
$$NO_2 + •OH + M \rightarrow HNO_3 + M^* \quad (6)$$

It should be noted, that in our opinion, N_2O_4 does not react with these radicals which are generated by dynamic cavitation of hydrogen peroxide solution (HOOH) [5].

What exactly does cavitation means? Cavitation is the generation, subsequent growth and implosive collapse of gas or vapor-filled bubbles in liquids when subjected to rapid changes of pressure and temperature [9].

Under title cavitation, in liquid, realize the formation of steam and gas filled cavities or bubbles in the local fluid pressure decreases to the vapor pressure (i.e. in the process of boiling cavities). The system, tends to homeostasis, trying to balance the pressure between the two phases. As a result, the pressure in the bubbles, rising slowly and the reverse of boiling - condensation on the walls of the cavity. During this time, the cavity is formed in technical vacuum. The surrounding liquid phase , trying to fill the "void", creates forces which are directed along the normal to the center of the cavity. During the collapse of the bubbles is a "micro-explosion" of the cavitation cavity, which is formed in the center of the high pressure and high temperature (in the hundreds or thousands of times higher than the standard condition).
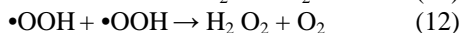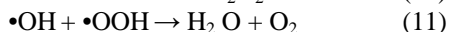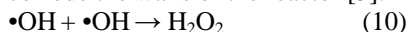
Hence, the energy release when bubbles collapse is sufficient for excitation, ionization and dissociation of molecular substances in the cavitation bubble.

During cavitation bubbles in the solution of moving the radicals •H, •OH ions and low energy electrons generated during the decomposition of substances in the cavitation bubble and the metastable excited states of molecules.

As previously indicated, hydrodynamic cavitation is the more energy-viable option in chemical engineering [5]. Subsequently, the means of generating radicals from hydrogen peroxide under the influence of hydrodynamic cavitation are shown:

$$H_2O_2 \rightarrow 2 \bullet OH \qquad (8)$$
$$H_2O_2 + \bullet OH \rightarrow H_2O + \bullet OOH \qquad (9)$$
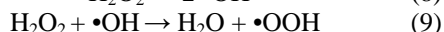
Because of their high reactivity radicals may interact with themselves and corrode the walls of the reactor [5]:

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \qquad (10)$$
$$\bullet OH + \bullet OOH \rightarrow H_2O + O_2 \qquad (11)$$
$$\bullet OOH + \bullet OOH \rightarrow H_2O_2 + O_2 \qquad (12)$$

Therefore, as a material for the reactor, we use a glass.

It is well known that hydroxyl radicals because of its high reactivity and short lifetime ($\tau \approx 10^{-8}$ c) can only interact with reagents entourage. From our point of view, the presence of water promotes the transfer of the radicals throughout and increases the lifetime τ [5]:

$$\bullet OH + H_2O \rightarrow HO\text{--}H\text{--}OH \rightarrow H_2O + \bullet OH \qquad (13)$$
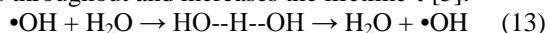
The mechanism of this "spillover" on the reaction volume, we characterize as a spillover •OH radicals in the aquatic environment. The term spillover first proposed by M. Boudart [10] for the transport process (diffusion) of adsorbed hydrogen on the surface of the catalyst.

Based on these ideas, we carried out a B3LYP/6-311++G(3df,3pd) calculation of TS of process (13): •OH radicals spillover in the gas phase with water vapor. The calculation results yield very low activation energy ($E_a = 14.7$ kJ) of process (13), which indicates a real possibility to the OH radicals transfer over the reaction volume.

Experimental part. In the experimental part, we were faced with the following objectives: to confirm that the formation of nitric acid without surface mechanism is no possible; synthesizing HNO_3 without absorption NO_2 by water; intensification for nitric acid formation by dynamic cavitation. . In Fig. 3, the laboratory unit to carry out the experiments for nitric acid formation is shown.
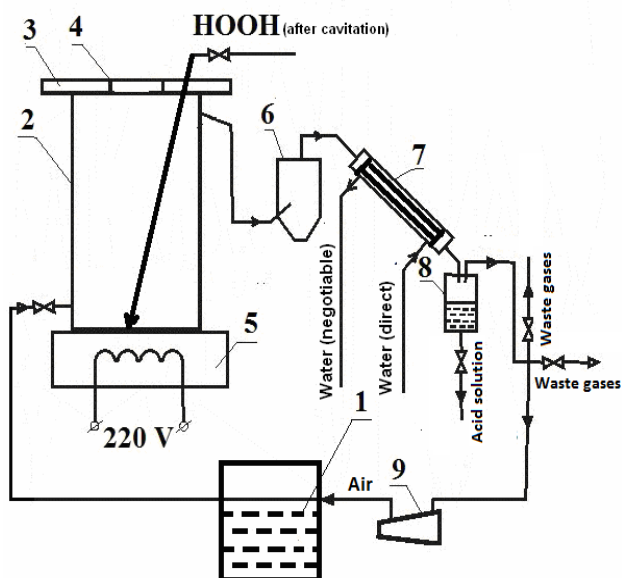

Fig. 3. Laboratory unit scheme for nitric acid formation:
(1) NO_x generator, (2) Reactor, (3) Lid, (4) Quartz glass, (5) Electric oven, (6) Refrigerator condenser, (7) Heat exchanger, (8) Container for analysis, (9) Compressor

Hydrogen peroxide after ultrasonic cavitation was dripped into the reactor where at a temperature was over 100° C and generated •OH and •OOH radicals (see Eqs. 8–9) are interacted with NO_x (by Eqs. 5–6). The oxides of nitrogen (generated by Kipp's apparatus) were pumped through the reactor with the help of the compressor. The resulting liquid-gas mixture was pre-heated by allowing it flow through the heat exchanger so as to efficiently transfer heat from one medium to another, which is then finally fed into a measuring vessel for analysis.

The experimental time was ~ 30 min. During this period, iron, whose synergistic effect mainly is the production of additional •OH radicals, was completely dissolved. The concentration of acid decreased from 56 % to 34 %. The quantity of nitric acid formed in the experiment using hydrogen peroxide corresponds to ~ 14.5 % of the quantity of the trapped NO_x. Therefore, the cavitation-procedure can increase nitric acid formation to ≈ 20 %, the calculated error in the experimental data was 5 % [5].

Based on this result, we present an industrial approach as illustrated in scheme (Fig. 4) [11].
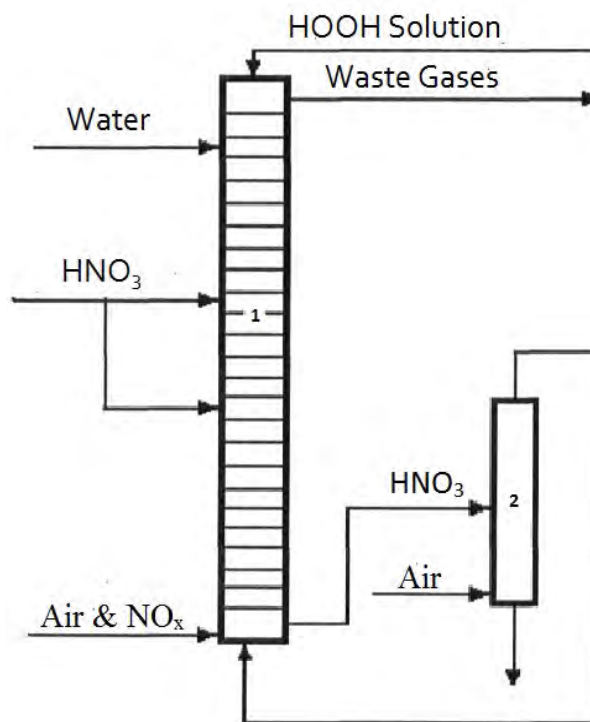

Fig. 4 Industry unit scheme for nitric acid formation:
(1) Absorption Towe, (2) Pumping Tower

In our opinion, this technological approach can be quite useful for the present chemical industry which completely rules out the catalytic-purification stage.

III. Waste Materials

As stated above that solid-wastes during nitric-acid production contains deactivated catalysts, they can however, be utilized at the solid-wastes disposal. Further, some of them may be sent to the recycle to obtain coast compounds from catalyst. But unfortunately, it has not

quite been a successful technique. From our view-point, this calls for a catalyst-replacement, and carefully use energy from hydrocarbons more because during the ammonia-oxidation step at the plant, heating the flow to 900° C [4] is an absolute waste of energy.

We, therefore, propose a more-efficient method for the oxidation of ammonia [12] which is based on electrically conducting catalyst (ECC). In contrast to convectional technology, this method does not require heating through-out the whole-phase. ECC heats only itself and the reaction space around. Also, ECC does not need any precious or rare metals. It can use metals with high degree of electrical-resistance. We, therefore, recommend for this type of catalyst a mixture of nickel (Ni) and chrome (Cr) [12]. In Fig. 5, a laboratory unit to carry out experiments with an ECC is shown.
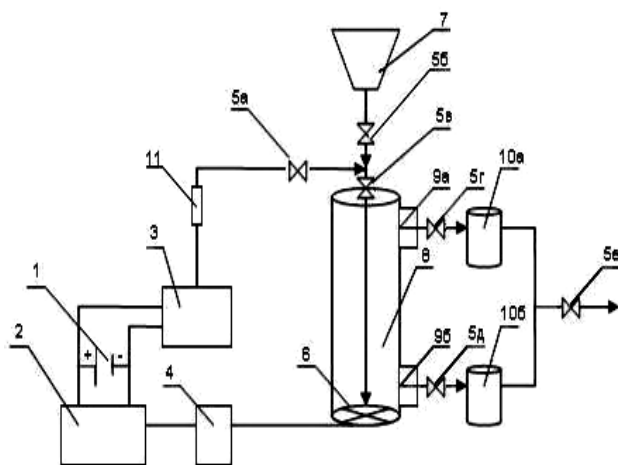

Fig. 5. laboratory unit to carry out experiments with ECC:
(1) AC power supply, (2) laboratory autotransformer (LATR),
(3) the compressor, (4) Ammeter, (5a-e) cranes, (6) ECC,
(7) tank for ammonia solution, (8) reactor made
of quartz glass, (9) analytical point,
(10) tanks for sampling,
(11) flowmeter

Unfortunately in this moment we could not present an experimental data, but we still work in this field

Conclusion

This paper is intended to solve the problem of creating environmentally friendly technology for the nitric acid production. On the basis of existing production the analysis of produced waste and methods of disposal was carry out. The new technological solutions for the chemical industry that will achieve a low or non-waste technology is a cavitation of HOOH. Thus, due to the intensification of the absorption step, it is possible to increase the yield of the final product (HNO_3) by 20 % and reduce emissions of gaseous wastes to levels appropriate sanitary norm without further purification. In our opinion, this technological approach can be quite useful for the present chemical industry which completely rules out the catalytic-purification stage.

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