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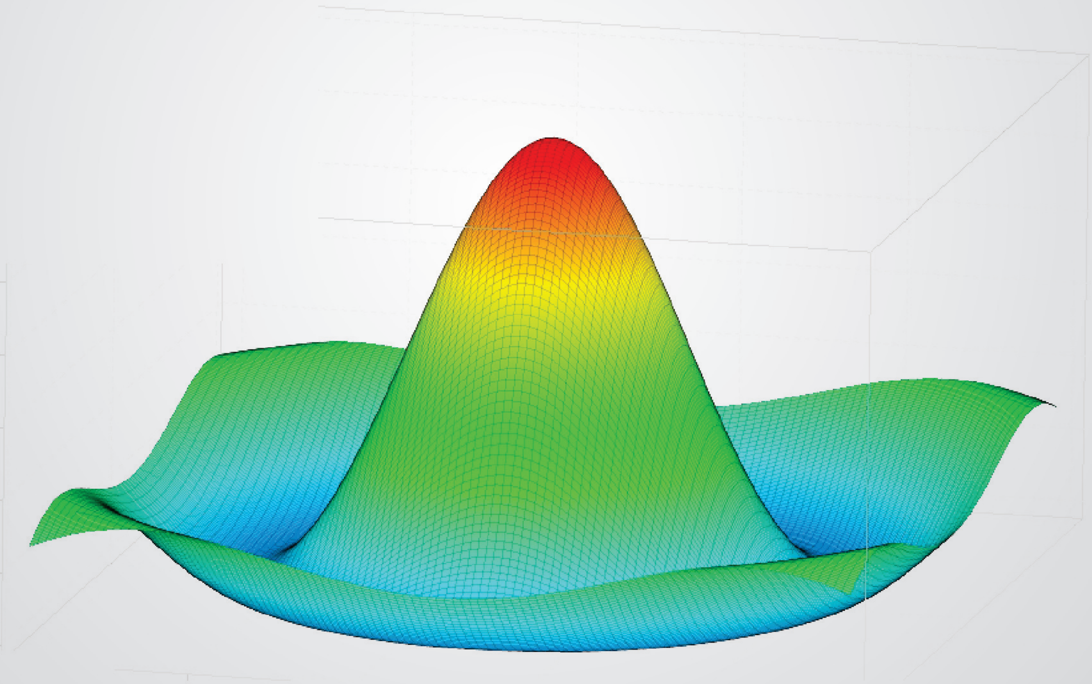

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WAYS OF REDUCING NITROGEN OXIDES IN THE DRYING AGENT TO IMPROVE BEET PULP QUALITY

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Abstract: *The article deals with the analysis of nitrogen oxides NO_x formation in the agent for beet pulp during combustion process of various fuels. Various methods of reducing the nitrogen oxides concentration, formed in the fuel combustion conditions at high temperatures, are given. It is established that the output of nitrogen oxides during gas combustion is mainly determined by the maximum temperature of the combustion products and their rate of cooling. It is shown that the nitrogen oxides toxicity determines the overall level of toxicity of combustion products of coal and fuel oil on 40...60 % and 92…98 % of natural gas. Radical method to eliminate NO_x is a noncontact method of preparation of the drying agent.*

Key words: beet pulp, drying agent, combustion, heat- generator, nitrogen oxides

I.Introduction

Beet pulp is a valuable high carbon product. It cannot be stored fresh for a long time, therefore it is dried and granulated for storage and transportation. The dried product contains, %: protein – 7…9, cellulose – 19…23, nitrogen-free extractive substances – 55…65, fat – 0,3…0,5. Dried beet pulp compared with fresh has the following advantages: it is more (7…8 times) nutritious than fresh; less deteriorates during storage; more transportable, especially in granular form; its transportation costs, in comparison with fresh pulp, decrease by more than 5 times [6]. Determining factor in production process of dry beet pulp is its drying method, providing soft temperature mode using heat-transfer agent with a minimum content of pollutants (mainly nitrogen oxides) from fuel combustion products. There are chemical transformation of components of pectin containing raw materials during the drying process, which can significantly affect its quality. Beet pulp is rich in high-polymeric substances: proteins, carbohydrates and lipids.

There are structural changes under the influence of temperature with the formation of new compounds, including nitrosamines during the pulp drying. Thus, beet pulp contains up to 25 mg/kg of amino acids and the drying agent – nitrogen oxides, which are major components of nitrate formation during the drying process. Therefore, one of the most important task is the neutralization of nitrogen oxides formed during fossil fuel combustion.

The most important elements of installations for beet pulp drying are generators for the preparation of drying agent, which are divided into contact and contactless depending on the method of preparation [2, 7, 8]:

– contact consist of a combustion chamber and a mixing chamber where it is mixed fuel combustion products with atmosphere air in the ratio, which provides predetermined temperature of drying agent;

– contactless generators assume heating of the air through the dividing surface of steam heat exchange and combustion products of liquid or gaseous fuel which is implemented in regenerative heaters – steam air and fired air heaters.

Currently used steam air heaters are not satisfactory because of leakage due to hydraulic shocks, condensation freezing in the winter period when the steam supply failure take place. It makes to replace industrial steam air heaters for non-serial heaters made of steel pipes and cast-iron economizer elements. Such reconstructions are bulky and metal-intensive. Therefore, where it might be advisable to use water heaters. In some cases installation of steam air heaters can't be done without high capital costs due to the lack of necessary facilities of steam boilers, networks for transportation of the heat carrier to the drying section and condensate drain. Operation of the existing fired air heaters is ineffective because of their bulky and inefficiency [9]. At combustion of hydrocarbon fuel in the composition of the flue gases there are formation of highly toxic nitrogen oxides NO_x (sum of NO and NO_2), carbon monoxide CO, unburned hydrocarbons and products of incomplete oxidation (aldehydes, ketones), sulfur oxides SO_x (sum of SO_2 and SO_3), as well as solid aerosol particles, which may contain various chemical compounds, including carcinogenic substances (for example, benzpyrene C20H12). The formation of NO_x, SO_x and CO happens with the passage of high-temperature combustion processes; SO_3 and aerosols formation also depends on the chemical composition of the fuel and method of its preparation. [14]. The drying agent, prepared in fired air heaters, has a high content of nitrogen oxides, which leads to the increase of nitrosamines in the pulp. The design of modern air heaters is rather compact system of pipes and tubular plate sections, part of which is made of alloy stainless steel and another part for temperatures less than 300 °C is made of borosilicate glass with special sealing materials. The flue gas leaving temperature is decreased to 40…45 °C in these devices. Through the use of condensation heat of water vapor part, located in the flue gases, additional saving heat is achieved up to 10 %. However, the introduction of such devices is not always possible due to the significant cost or local nature reasons (existing heat supply systems, drier design, production areas).

Thus, both methods are promising to obtain a drying agent: contactless – to ensure high thermal characteristics and contact – to exclude the formation of significant amount of nitrogen oxides in combustion products. Therefore, the process of fuel combustion in furnaces should be organized so that to provide minimum emission of nitrogen oxides with leaving gases and total fuel burnout through a combination of operational factors and the use of special measures.

Results and discussion

Natural gas is used as a fuel in most modern heat generators. There are kinetic, diffusion and mixed principles of gas-air mixture combustion in accordance with the method of gas fuel mixing with oxidant. Kinetic [15] combustion of gas-air mixture involves premixing of gas with required amount of air for its complete combustion, that provides homogeneous gas-air mixture combustion with excess-air coefficient. Full gas combustion time τ_k during kinetic combustion is restricted to the time needed for mixture heating and gas ignition τ_{inf}, and also high-temperature oxidation time of gas from the time of ignition until the time of completion of the chemical reactions τ_c:

$$\tau_k = \tau_{inf} + \tau_c. \qquad (1)$$

Kinetic principle is applied in cases when you need to burn fuel with high thermal stresses without heat loss due to incomplete combustion, that takes place in relatively small plants [13]. In contrast to this method, fuel gas and air can be suppressed to the combustion chamber separately. In this case, each particle of gas can only react provided that particle of oxygen will be delivered to it. Therefore, if we heat gas to high enough temperature, burning will start at the surface boundary, separating gas and air. New and new components will be involved in the reaction as a result of the mutual diffusion between reactive components. Such gas combustion, where the processes of combustion and formation of the mixture occur simultaneously, is called diffusion.

It is obvious that we will need more time to complete the combustion process during diffusion combustion, than during kinetic combustion on the amount of time necessary to mix the components τ_m. Then the complete gas combustion time during diffusion combustion is:

$$\tau_д = \tau_{inf} + \tau_c + \tau_d. \qquad (2)$$

The gas can also be premixed with a part of the air required for combustion, and the missing quantity submitted additionally to the furnace volume. This combustion principle of pre-mixed gas mixture with excess-air coefficient $\alpha' < 1{,}0$ is called mixed principle [8]. When it is compared with the kinetic and diffusion principles, the time of complete combustion takes an intermediate value. This principle is used in household installations.

Expected heating time of the mixture τ_i and chemical reaction time τ_c are negligible in the furnace volume at high temperatures [8] compared with the time spent on mixture formation τ_m

$$\tau_m \geq \tau_{inf} + \tau_c \qquad (3)$$

and the combustion process is almost completely dependent on the time of mixture formation

$$\tau_k \approx \tau_m. \qquad (4)$$

Enough investigations of the nitrogen oxide formation process during gas combustion have been currently carried out. There are three known mechanisms of nitrogen oxide formation, in accordance with them nitrogen oxides are classified as thermal, fuel and fast.

NO_x is formed from T_{max} to $T_{max} - \Delta T$ □(on both sides of the maximum) at a temperature $T_{max} - \Delta T$ during gas combustion. According to [8], the torch can be divided into three zones:

the initial ($T < 1800$ K), where hydrocarbon burning and fast and fuel nitrogen oxide formation take place;

the second, located on both sides of the plane of maximum temperatures, where thermal nitrogen oxide formation take place;

the third, the tail area of the torch; nitrogen oxides are not formed, moreover – their partial recovery is possible.

Thermal NOx are formed as a result of chain reactions in flames, where molecular nitrogen is oxidized by atomic oxygen [5].

According to this mechanism, the basic amount of nitrogen oxides is formed in the burning zone at the maximum temperature (at $T > 1900$ K).

It is characterized by the following reactions, kJ / mol:

$$O + N_2 \rightarrow NO + N - 314; \quad (5)$$

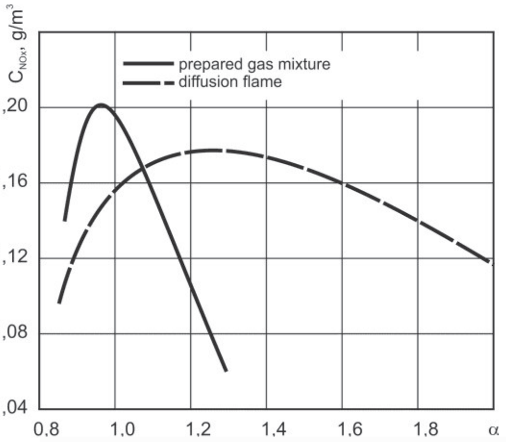
$$N + O_2 \rightarrow NO + O + 134. \quad (6)$$

Maximum NO_x output during kinetic gas combustion is respectively $\alpha \approx 0{,}9\ldots1{,}0$ (see figure). For turbulent diffusion gas combustion the maximum concentrations of nitrogen oxides are $\alpha = 1{,}1\ldots1{,}2$ and curve $C_{NOx} = f(\alpha)$ is characterized by a weak dependence on excess-air coefficient. Temperature and reaction time, characterized by warm cooling in the zone of maximum temperatures, have a decisive influence on the formation of thermal NO_x.

$$NO_x^{therm} = f_1(T_{max}, \tau_p) = f_1(T_{max}, dT/d\tau). \quad (7)$$

The output of thermal NO_x at cooling rate of the combustion products 104…105 K/s is 0,1…0,3 g/m^3 in the small-sized exact cameras without air heating.

Fuel nitrogen oxides are formed during the combustion of nitrogen-containing fuels in the zone of relatively low temperatures ($T > 1000$ K). Their output is practically independent of temperature.



The graph of nitrogen oxide concentration dependence on excess-air coefficient

There is an increase in fuel NO_x output with the increase of atomic oxygen concentration in combustion zone. Fuel nitrogen oxides are not formed during the natural gas combustion.

Fast nitrogen oxides are formed in the tail part of a torch, where the temperatures are relatively low. The experiments [5] showed that the reaction mechanism of hydrocarbon radicals with nitrogen molecule acts in this combustion zone, Kj/mol:

$$CH + N_2 \rightarrow HCN + N - 8{,}4. \quad (8)$$

The studies [10] confirm the formation of fast NO_x in the combustion zone.

The output of nitrogen oxides during gas combustion is mainly determined by the maximum temperature of the combustion products and their cooling rate. In diffusion torch nitrogen oxides are formed more intensively in comparison with kinetic method of gas combustion, since the time of complete oxidation of its components in this case is smaller.

As a drying agent, received in contact-type heat generator, contains nitrogen oxides, the radical method to eliminate nitrosodimethylamine in the pulp is non-contact method for preparation of the drying agent [3]. But currently operated heaters are not satisfactory, moreover their installation requires large capital costs for reconstruction of steam producing capacities and the laying of heat pipelines. Heat consumption for drying increased by 20…25 %.

The use of existing heaters is not profitable because of their low performance, bulkiness and high metal content [1]. Along with high technical and economic performance of fire heaters, we should note the high price of the materials used for their manufacture. From technical and economic considerations, it is reasonable to use contact-type heat generators provided that nitrogen oxide content decreases in the products of natural gas combustion. Nitrogen oxides are part of the toxic substances contained in products of any fuel combustion. The main indicator of combustion product toxicity T is the ratio of the concentrations of the toxic substance in combustion products C_i to one-time maximum permissible concentration of the substances in the atmospheric air MAC [16]. For example, for nitrogen dioxide

$$T_{NO_x} = \frac{C_{NO_x}}{MAC_{NO_x}} = \frac{C_{NO_x}}{0{,}085}. \quad (9)$$

Under the joint effect of several toxic substances there is additive effect:

$$T = \frac{C_{NO_x}}{MAC_{NO_x}} + K_i \frac{C_i}{MAC_i}. \quad (10)$$

The study of the content of harmful substances in products of fuel combustion gives an estimate of the main toxic substances in products of some fuel combustion and the contribution of nitrogen oxides in the general toxicity level of products of fuel combustion (see table).

Toxic concentration in combustion products, g/m^3 and their toxicity level C/MAC (in parentheses).

Furnace substance	**Fuel**		
	Coal	**Fuel oil**	**Natural gas**

	(S = 1,7 %)	(S = 2,3 %)	
Sulfur oxides in terms of SO_2	3,0 (6000)	4,0 (8000)	traces (0)
Nitrogen oxides in terms of SO_2	0,25…1,5 (2900…17600)	0,25…1,5 (2900…17600)	0,2…1,8 (2300…21000)
Ash, dust	0,06…0,10 (120…2000)	0,07…0,35 (140…700)	0,0…0,07 (0…140)
Carbon oxide	0,02…0,30 (4…60)	0,05…0,50 (10…100)	0,01…0,10 (2…20)
Aldehydes in terms of SO_2	– –	0,05…0,50 (10…100)	0,01…0,10 (2…20)
Soot	0,035…0,070 (230…460)	0,001…0,100 (70…700)	0,0075…0,015 (50…100)
Benzpyrene (10^8)	10…50	2…30	0…2
C_2OH_2	100…500	20…300	0…20

From this table we can see that the toxicity of nitrogen oxides determines the total toxicity level of products of coal and fuel oil combustion by 40…60 % and 92…98 % of natural gas.

Reducing method of nitrogen oxide content in the combustion products through their recirculation is used. This method allows to reduce the maximum temperature in the flame core by 100…130 K and reduce NO_x output twice when the degree of recirculation is $r = 20$ % [12].

Reducing method of nitrogen oxide content in the flue waste gases by moisture metering into the combustion chamber in the form of steam, water or steam-water mixture alows to reduce NO_x concentration in the combustion products by 20…25 %, but it reduces efficiency of the installation. In addition, this method is not widely used in the facilities for drying agent preparation, as during the mixing of flue gas with atmospheric air ((before drying installation), the drying agent has a high moisture content, which has an adverse effect on the technical and economic performance of drying process and humidity of the finished product.

You can decrease the nitrogen oxide content in flue gas to 39…48 % with the help of sulfur fuel combustion or artificial introduction of sulfur in the product of gas combustion [4] as sulfur is more reactive than nitrogen with respect to atomic oxygen. And nitrogen dioxide recovery takes place, Kj/mol:

$$NO_2 + SO_2 \leftrightarrow NO + SO_3. \quad (11)$$

The disadvantage of this method is the corrosive effect of sulphur dioxide on the equipment. The use of fuels, containing sulfur in elevated amounts (for example fuel oil) as a drying agent in heat generators can cause spotting of dry pulp. There is a method of reducing NO_x output by two-stage combustion of gas fuel. Part of the air, required for combustion, is premixed with gas, which leads to lower temperature and reducing oxygen concentration in the primary combustion zone. The remaining air is used for post-combustion of the mixture. In the initial zone the fuel is burned with the lack of air ($\alpha < 1$), that allows to reduce the temperature by100...130 K**.** In the second combustion area, where oxygen is present in excess, the temperature level is lower than during combustion of stoichiometric mixture. The described method allows to reduce NO_x output approximately by half.

The method of stack gas cleaning from nitrogen oxides is used by submission of ammonia in the temperature zone ~ 1200 K without catalyst, or at ~ 650 K- with the use of vanadium catalysts, for ammonia recovery [11]. The content of nitrogen oxides is reduced by about five times. The application of this method it is not possible in the units of the drying agent for food processing, as the presence of ammonia affects the toxicity of the drying agent. In addition, this method is more expensive than the others in 10…30 times.

There are also other methods of reducing nitrogen oxide content in the products of gas combustion, but their effectiveness is not higher than listed.

The output of nitrogen oxides is caused mainly by maximum temperature of the combustion products and their rate of cooling. As a drying agent, obtained in contact-type heat generators, contains nitrogen oxides, a radical method for nitrosamine elimination in products is a non-contact method of drying agent preparation. But currently operated heaters are not satisfactory, their installation requires large capital investments for reconstruction of steam producing capacity and the laying of heat pipelines. Moreover, the heat consumption for drying increases by 20…25 %.

Conclusions

Structural changes with the formation of new compounds, including nitrosamines, occur in the drying process of beet pulp under the influence of temperature. The main components of nitrates formation are considerable content of amino acids in the pulp and nitrogen oxides in the drying agent.

Therefore, one of the most important tasks is to neutralize the oxides, formed during fossil fuel combustion. A decisive influence on the formation of thermal NO_x provide temperature and reaction time, which is characterized by warm cooling in the area of maximum temperature of heat generators. The toxicity of nitrogen oxides determines the overall toxicity level of products of coal and fuel oil combustion to 40…60 %, and to 92…98 % of natural gas combustion. The output of nitrogen oxides in heat generators is mainly caused by the maximum temperature of the combustion products and their rate of cooling. As the drying agent, obtained in the contact-type heat generators, contains nitrogen oxides, a radical method for elimination of nitrosamines in products is the non-contact method of the drying agent preparation, but its installation requires large capital costs for reconstruction of steam producing capacity and the laying of heat pipelines. The heat consumption for drying increases by 20…25 %.

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