Academicia Globe: Inderscience Research

ISSN: 2776-1010 Volume 4, Issue 4, April, 2023

ANALYSIS OF THE COMPOSITION OF GASES IN THE SYNTHESIS OF CALCIUM CYANAMIDE

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Annotation

Technical solutions have been developed to create a technology for the production of calcium cyanamide from lime, carbonate anhydride and industrial ammonia. A technological scheme for the production of nitrogen fertilizer and an effective defoliant - calcium cyanamide has been developed and the optimal technological parameters of the process have been determined at the experimental plant. An experimental batch of calcium cyanamide has been produced.

Keywords: Carbon dioxide, ammonia, expander gas, calcium cyanamide, off-gases.

Temperature is one of the most important technological parameters of calcium cyanamide synthesis which is the most important primary energy expenditure in the carbide-free method.

For further analysis and absorption of exhaust gasses in the experimental device, the following was done:

- With a 10% reserve, a 7 N sulfuric acid solution was added to the absorber for 15 minutes in the amount of gas mixtures.
- With a 10% reserve, it was placed in the absorber for 15 minutes in the amount due to the release of gas mixtures from the 40% NaOH solution.
- Absorbers are replaced with their contents every 15 minutes.
- Absorbed off-gases in the absorber are collected through a gas counter into the uldar gas collector for total volume measurement.

As a result of the research, a granular white product was obtained. The volume of the product is reduced compared to the initial volume of the product, its strength is higher compared to the initial volume. The white color in the resulting product confirms the absence of free carbon. The obtained calcium

ISSN: 2776-1010 Volume 4, Issue 4, April, 2023

cyanamide was qualitatively analyzed depending on the content of CO_2 and CN^{-1}- ions. The result of these analyzes showed that CO_2 and CN^{-1}- ions were not present definitely. The nitrogen content in the synthesized calcium cyanide depends on the process temperature.

From the obtained data, it can be seen that the retention of nitrogen in the obtained product reaches a maximum at the beginning and increases to 30.2% at 800° C (Figure 1). At 900° C, its growth decreases. The lack of nitrogen below the temperature of 800° C is caused by the incomplete reaction during the synthesis of calcium cyanamide, and its low amount with increasing temperature is caused by the thermal decomposition of ammonia, which is one of the initial components, above the temperature of 800° C. The change in nitrogen content of the obtained product corresponds to the results of [2].

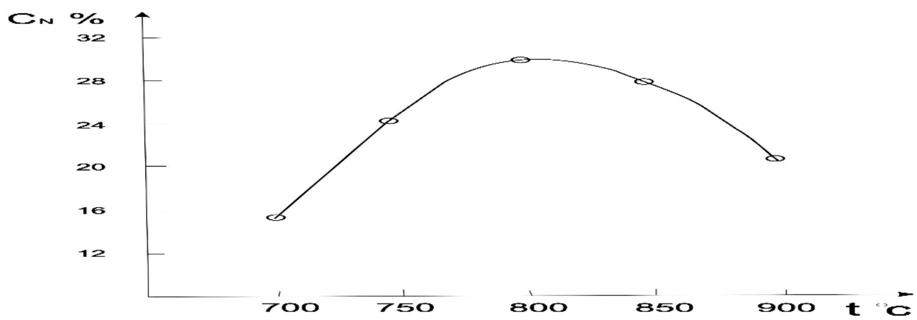

Figure 1. Dependence on temperature of the amount of nitrogen in the product.

It should be noted that carbon dioxide gas is found in the product at temperatures below 800° C.

This is due to the fact that the chemical reaction in the partial formation of calcium carbonate gas under the given conditions is as follows:

$CaO+CO_2=CaCO_3$ (1)

At temperatures of 800° C and above, under hermetic conditions, the equilibrium of this reaction shifts to the left, and therefore the presence of calcium carbonate in the obtained products was not seen.

According to the literature review, a number of gaseous components may be involved in the synthesis of calcium cyanamide, the presence of which depends on the used starting materials and a number of processes involved in the production of calcium cyanamide. Carbon monoxide, carbon dioxide, ammonia, hydrogen cyanide, nitrogen, hydrogen, water vapor, etc. are found in the gases emitted by the above-mentioned factors[3-4].

The effect of substances which consist of composition and quantity of emitted gases was determined by stoichiometric calculation according to the reaction:

$$CaO+2NH_3+CO_2=CaCN_2+3H_2O \quad (2)$$

During the synthesis of calcium cyanamide, an increase in temperature reduces the amount of ammonia and carbon dioxide, and the amount of ammonia decreases relative to carbon dioxide. As the

ISSN: 2776-1010 Volume 4, Issue 4, April, 2023

temperature increases from 700 to 900°C, the amount of ammonia decreases to 7.46% and that of carbon dioxide decreases to 0.60%. With the increase in temperature, the amount of nitrogen in the gases emitted by the synthesis of calcium cyanamide from 700 to 900°C increases by 2%, and that of hydrogen increases by 6%.

When it comes to carbon monoxide, its amount is minimal and practically does not depend on temperature.

The amount of carbon monoxide in the range of temperatures can be up to 0.18-0.25% (Figure 5).

The amount of methane in the emitted gases is in the range of 0.22-0.31% (Figure 6).

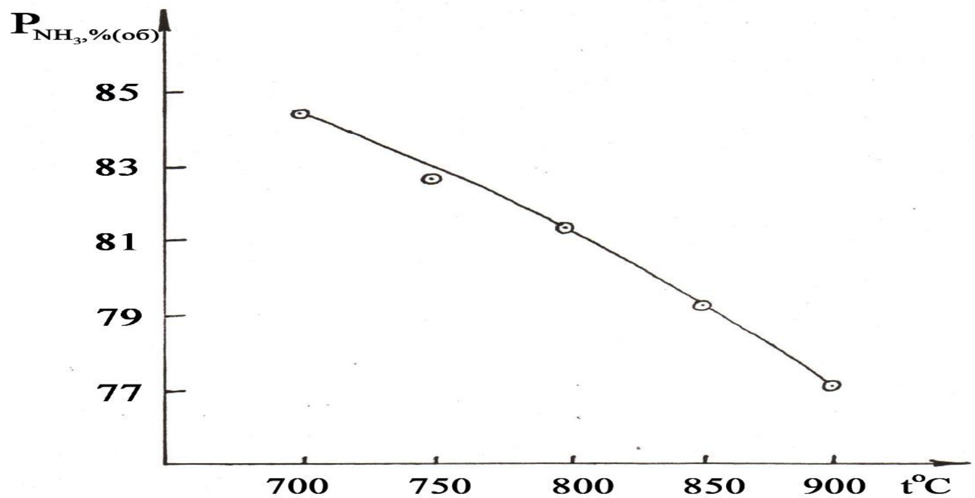

Figure 2. Dependence on temperature of carbon dioxide in the exhaust gases' content.

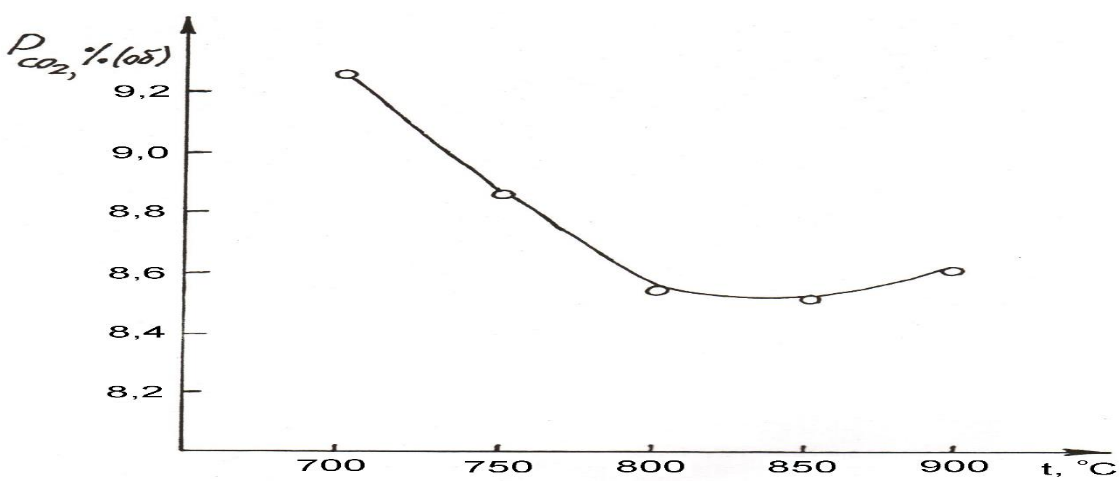

Figure 3. Dependence on temperature of nitrogen in the exhaust gases' content.

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ISSN: 2776-1010 Volume 4, Issue 4, April, 2023

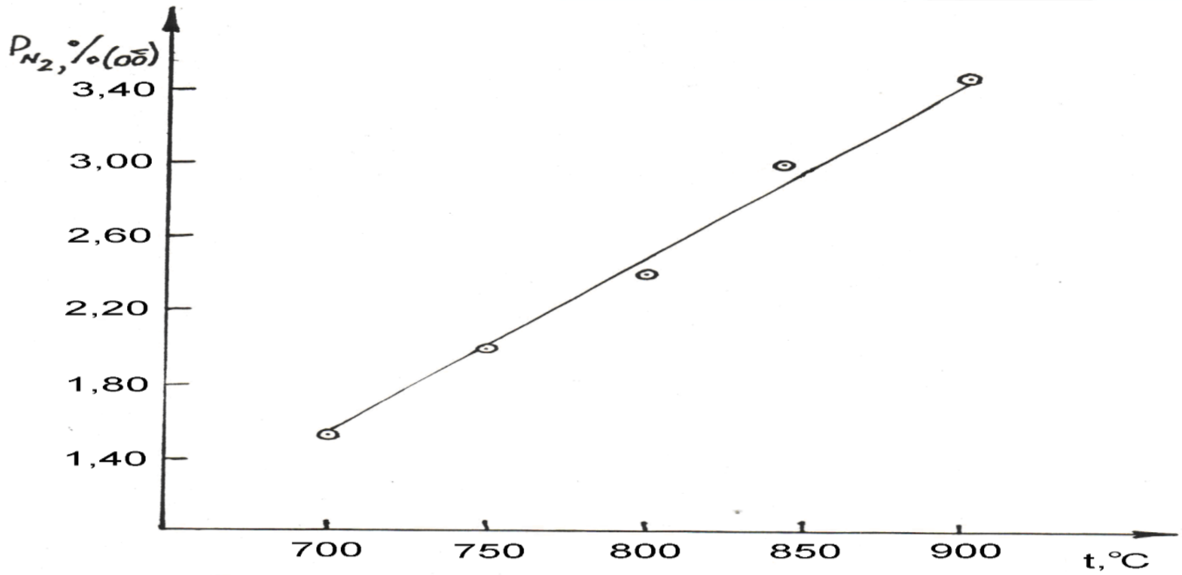

Figure 4. Dependence on temperature of hydrogen in the exhaust gases' content.

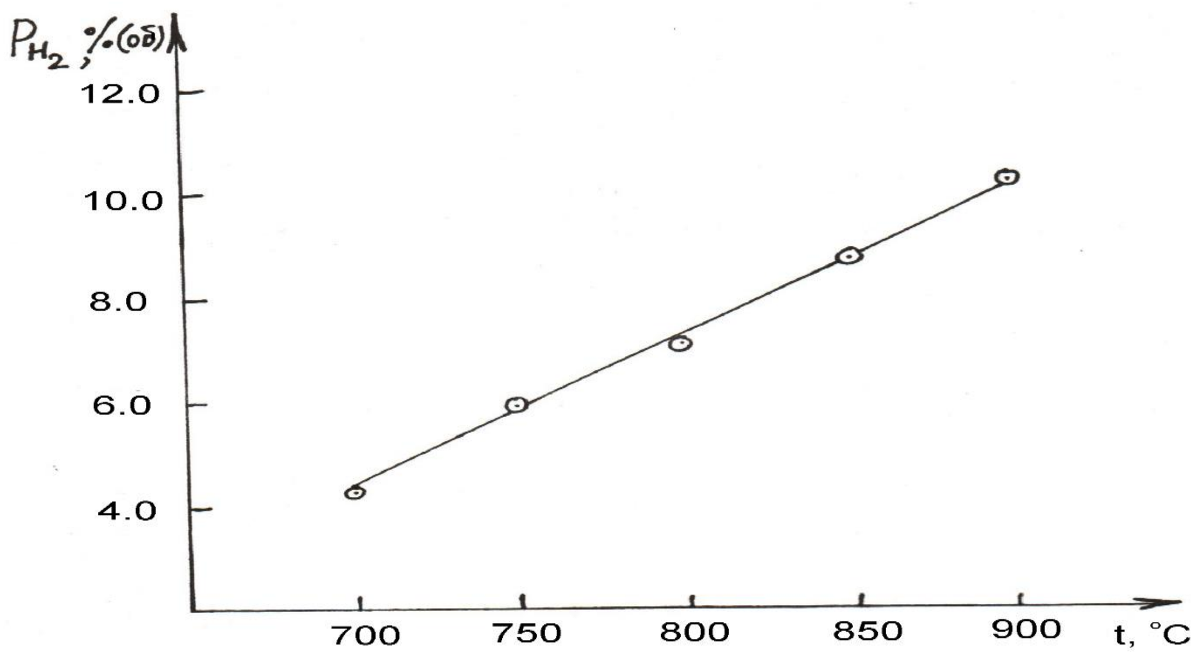

Figure 5. Dependence on temperature of carbon monoxide in the exhaust gases' content

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ISSN: 2776-1010 Volume 4, Issue 4, April, 2023

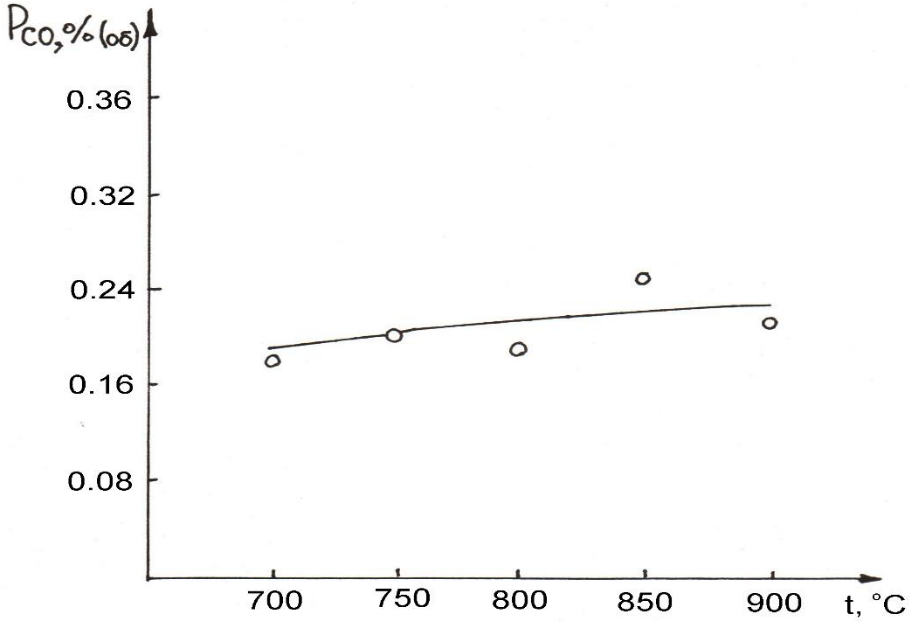

Figure 6. Dependence on temperature of methane in the exhaust gases' content.

The content of gaseous compounds used for the synthesis of calcium cyanamide is very small, and they are carbon monoxide and methane compounds, not additional reaction products.

$$CO_2+2NH_3=CH_4+H_2O+N_2+0{,}5O_2 \quad (6)$$

As shown in Figure 2, the content of carbon dioxide in the exhaust gases decreases when the temperature of calcium cyanamide synthesis is increased from 700 to 800oC.

After increasing the temperature above 800oC, it first increases and then decreases with increasing temperature.

The reduction of nitrogen content in the product in Figure 3 results in the carbon dioxide reacting chemically to form a small amount of calcium cyanamide.

Experimental studies on the effect of temperature on the synthesis of calcium cyanamide show that as soon as the temperature increases, the amount of nitrogen in the product reaches a maximum at 800oC, and the nitrogen content decreases with further temperature increase. In all experiments, the product obtained was white, confirming the absence of free carbon. The product has been formed in the form of solid granules and has been 32% at the optimum temperature of 800° C, that is practically 1.5 times more than that of calcium cyanamide by the carbide method.

The analysis of the composition of the gases discharged from the reactor was studied, in which the content of ammonia and carbon dioxide decreases with the increase of synthesis temperature, which content of ammonia decreases more than carbon dioxide. The content of carbon monoxide and methane in the exhaust gases is minimal (ranging from 0.19 to 0.31%), and carbon monoxide and methane are not considered as some non-existent reaction products.

In conclusion, in the temperature range of 873-1473°K, $CO_2+2NH_3=CH_4+H_2O+N_2+0{,}5O_2$ and $CO_2+2NH_3=C+N_2+2H_2O+H_2O$ thermodynamic calculations determined the values of the heat effect of

ISSN: 2776-1010 Volume 4, Issue 4, April, 2023

intermediate reactions in the synthesis of calcium cyanamide, in which endothermic and thermodynamic changes and changes in the energy of gypsum at 1043ºK its amount was equal to +202383,94 and +36290.80 J/mol.

The optimal conditions for obtaining calcium cyanamide in the carbide-free method were studied: lime slag-granulated, its size is 2-3 mm, the ratio T:J=1:1.5 when preparing slag; the ratio of gases is CO_2:NH_3=1:9; volume velocity of the initial gas mixture is 6000 h-1; the synthesis process takes 90 minutes; the temperature during synthesis is 800°C. As the temperature rises, the synthesis of calcium cyanamide, the amount of ammonia and carbon dioxide, the amount of gases released from the reactor, decreases.

The analysis of the released gases showed that it contains carbon monoxide and methane [0.19-0.31%], which cannot be considered as by-products.

Through kinetic studies of the production of calcium cyanamide, the order of its chemical reaction with respect to ammonia (0.7125) and carbon dioxide (0.416) was studied. It became clear from the order of the reaction that the stoichiometric equations of the reaction are not simple and the mechanism of the process is very complex. The results of the study showed that the formation of calcium cyanamide was carried out at a high rate in the initial period, and later, with the increase of time, the balance of the product output was maintained, and the reaction rate decreased.

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