



THE EFFECT OF TEMPERATURE ON THE SYNTHESIS OF CALCIUM CYANAMIDE AND THE COMPOSITION OF THE EXHAUST GASES

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ABSTRACT

For the first time thermodynamic calculations on rather new physical and chemical constants specify temperature of the beginning of thermal decomposition of ammonia, and also probability of collateral chemical reactions between ammonia and carbon dioxide. Influence on synthesis cyanamid calcium of the basic technological parameters is investigated. The structure of departing gases from a reactor of synthesis cyanamid calcium depending on temperature is studied. Kinetic researches of process of synthesis cyanamid calcium certain orders of chemical reaction on ammonia and carbon dioxide and is proved, that a limiting stage of process of synthesis cyanamid calcium is diffusion of initial gas components through a layer of a product.

The chemical industry in the Republic of Uzbekistan plays a key role in the agrochemical complex, its production is based on high technologies, and the products manufactured according to the nomenclature comply with international standards. Therefore, the development of the chemical industry is a priority for the modern development of the economy of the Republic of Uzbekistan [1].

One of the main factors in the intensification of the agrochemical complex is its chemicalization, primarily the widespread use and effectiveness of the use of mineral fertilizers.

It is known that the annual population growth of the Republic of Uzbekistan is about 3%, and the area of irrigated arable land does not increase due to the acute shortage of water, but, on the contrary, even decreases slightly.

Under these conditions, it is possible to provide food to the country's ever-growing population through chemicalization of agriculture, since each ton of mineral fertilizers provides an annual need for agricultural products of 5-6 people, and the cost of producing and using mineral fertilizers is paid back 2-3 times agricultural products. Therefore, around the world, the production of mineral fertilizers and chemical plant protection products is growing rapidly. If the consumption of mineral fertilizers in the world in 1994 - 1995 was 121.8 million tons, then by now this figure has reached more than 155 million tons [2] ..

To make up for these soil losses in the Republic, the corresponding demand for mineral fertilizers declared by the chemical industry is not being sufficiently fulfilled. The same applies to the range of mineral fertilizers produced.

The main assortment of nitrogen fertilizers produced in our Republic is ammonium nitrate, urea and ammonium sulfate. These fertilizers are physiologically acidic and their long-term use has led and leads to the artificial acidification of millions of hectares of agricultural land, which negatively affects the increase in crop yields.

In addition, in world practice, there is a tendency to abandon the use of ammonium nitrate, which makes up the bulk of the nitrogen fertilizers of the Republic, or to tighten the requirements for it for explosion safety, which makes it much more expensive. In this regard, there is an urgent need for scientific research to create effective explosion-proof alkaline nitrogen fertilizers [3].

Temperature is one of the main technological parameters for the synthesis of calcium cyanamide by the carbide-free method, which is the main component of energy costs.

The synthesis of calcium cyanamide at various temperatures was carried out under the following initial conditions:

1. The initial mixture was prepared on the basis of lime obtained by calcination from the chalk of the Kitab deposit.
2. The mixture is prepared on the basis of CaO .
3. The size of the granules of the charge is 2-3 mm.
4. The volume of the charge is 10 ml.
5. The weight of the initial mixture - on average was 4.82 g.
6. The drying temperature of the initial charge of 600°C .
7. The duration of the passage of the source gas mixture is 90 minutes.
8. The synthesis temperature is from 700 to 900°C at intervals of 50°C .
9. The ratio of CO_2 to NH_3 as 1: 9.
10. The volumetric velocity of the initial gas mixture of 6000 h^{-1} .

For the absorption and subsequent analysis of the exhaust gases resulting from experiments on the experimental setup shown in (Fig. 1), the following was done:

1. A 7 N solution of sulfuric acid was poured into the absorber in an amount based on the passage of the gas mixture for 15 minutes with a margin of 10%.

2. A 40% NaOH solution was poured into the absorber in an amount based on the passage of the gas mixture for 15 minutes with a margin of 10%.

3. Absorbers with contents were changed every 15 minutes.

4. Exhaust gases not absorbed in the absorbers were passed through a gas meter to measure their total volume and collected in a gas collector ..

As a result of the experiments, a white granular product was obtained. The volume of the product decreased in comparison with the volume of the initial charge, and its strength was higher than that of the initial charge. The white color of the obtained product indicates the absence of free carbon in it, which is a prerequisite for its processing into other derivatives.

The resulting calcium cyanamide was subjected to a qualitative analysis for the content of CO₂ and CN⁻ ion according to the methods and. The results of these qualitative analyzes showed a clear absence of CO₂ and CN⁻ ions.

The nitrogen content in the synthesized calcium cyanamide, depending on the process temperature, is shown in Table 1 and Fig. 1.

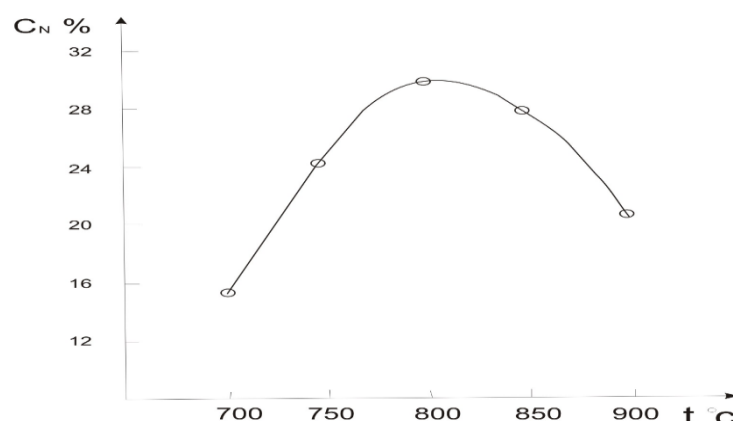
Table 1.

The nitrogen content in the product depending on the temperature of synthesis of calcium cyanamide

T _{синтеза} , °C	700	750	800	850	900
N ₂ , %	15,2	24,1	30,2	28,1	21,8

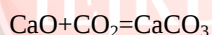
From the data obtained it follows that the nitrogen content in the obtained product initially increases with increasing temperature, reaching a maximum of 30.2% at 800 ° C, and with its further growth it begins to decrease. The relatively low nitrogen content at temperatures below 800 ° C is explained by the incomplete chemical reaction of the synthesis of calcium cyanamide, and a decrease in its content with an increase in temperature above 800 ° C is associated with the thermal decomposition of ammonia, one of the main starting components.

Fig 1. The dependence of the nitrogen content in the product on temperature



This pattern of changes in the nitrogen content in the synthesized product is practically consistent with the data [1].

It should be noted that in the composition of the product obtained at temperatures below 800 °C, the presence of calcium carbonate was detected. This is due to the fact that under these conditions, the following chemical reaction of the formation of calcium carbonate partially takes place:



At temperatures of 800 °C and higher under sealed conditions, the equilibrium of this reaction will shift to the left side and therefore the presence of calcium carbonate is not detected in the resulting product.

According to the data presented in the literature review, a number of gas components may be present in the composition of the exhaust gases from the process of synthesizing calcium cyanamide, the presence of which, first of all, depends on the type of the starting materials used and the number of processes occurring in the preparation of calcium cyanamide. Depending on the above factors, the composition of the exhaust gases may include carbon monoxide, carbon dioxide, ammonia, hydrogen cyanide, nitrogen, hydrogen, water vapor, etc.

The composition and amount of exhaust gases was determined by us according to the methodology, as well as by stoichiometric calculations of reacting substances by reaction $\text{CaO} + 2\text{NH}_3 + \text{CO}_2 = \text{CaCN}_2 + 3\text{H}_2\text{O}$ according to the nitrogen content found in the product.

Comparative data are given in table. 3 (in% to the volume of gas entering the reactor).

The composition of the exhaust gases from the reactor for the synthesis of calcium cyanamide from lime, ammonia and carbon dioxide (in terms of dry gas) is presented in table. 2, and changes in the content of each component of the exhaust gases depending on the temperature of synthesis of calcium cyanamide are presented in Fig. 2-7. As can be seen from the data table. 3, with increasing temperature of the synthesis of

calcium cyanamide, the content of ammonia and carbon dioxide decreases, and the content of ammonia decreases much more than carbon dioxide. Thus, with increasing temperature from 700 to 900 ° C, the ammonia content decreases by 7.46% (vol), and carbon dioxide only by 0.60% (vol). Obviously, this can be explained by a partial ammonia defixation, which is confirmed by an increase in the amount of nitrogen and hydrogen in the gases leaving the reactor. With an increase in the temperature of synthesis of calcium cyanamide from 700 to 900 ° C, the nitrogen content in the exhaust gases increases by 2.00% (vol), and hydrogen by 6.00% (vol).

Concerning the content of carbon monoxide, we can conclude that its amounts are minimal and practically independent of temperature. In the investigated temperature range, the amount of carbon monoxide ranges from 0.18-0.25% (vol).

Similar data were obtained on the content of methane in the exhaust gases, the amount of which varies in the range of 0.22-0.31% (vol).

Table 2.

The effect of temperature on ammonia and carbon dioxide balances.

TemperatureS ynthesis, oC	Contained. Nitrogen in the product, %	Ammonia balance (in% of the original)			The balance of carbon dioxide (in% to the original)	
		Inproduct	Indeparting. Gazah	Defix.	Inproduct	Inrel. Gazah
700	15,2	1,30	95,40	3,30	5,84	94,16
750	24,1	2,24	93,25	4,51	10,12	89,88
800	30,2	2,98	91,62	5,40	13,42	86,58
850	28,1	2,72	90,56	6,72	12,24	87,76
900	21,8	1,99	89,94	8,07	8,96	91,04

Table 3.

THE COMPOSITION OF THE EXHAUST GASES DEPENDING ON THE TEMPERATURE OF
THE SYNTHESIS OF CALCIUM CYANAMIDE.

Temperature °C	Components of the exhaust gas, % (vol)					
	NH ₃	CO ₂	N ₂	H ₂	CO	CH ₄
700	84,48	9,26	1,46	4,37	0,18	0,25
750	82,72	8,86	2,00	6,00	0,20	0,22
800	81,37	8,54	2,40	7,19	0,19	0,31
850	79,23	8,53	2,94	8,82	0,25	0,23
900	77,02	8,66	3,46	10,37	0,21	0,28

Fig. 2. The dependence of the content of ammonia in the exhaust gas from the temperature

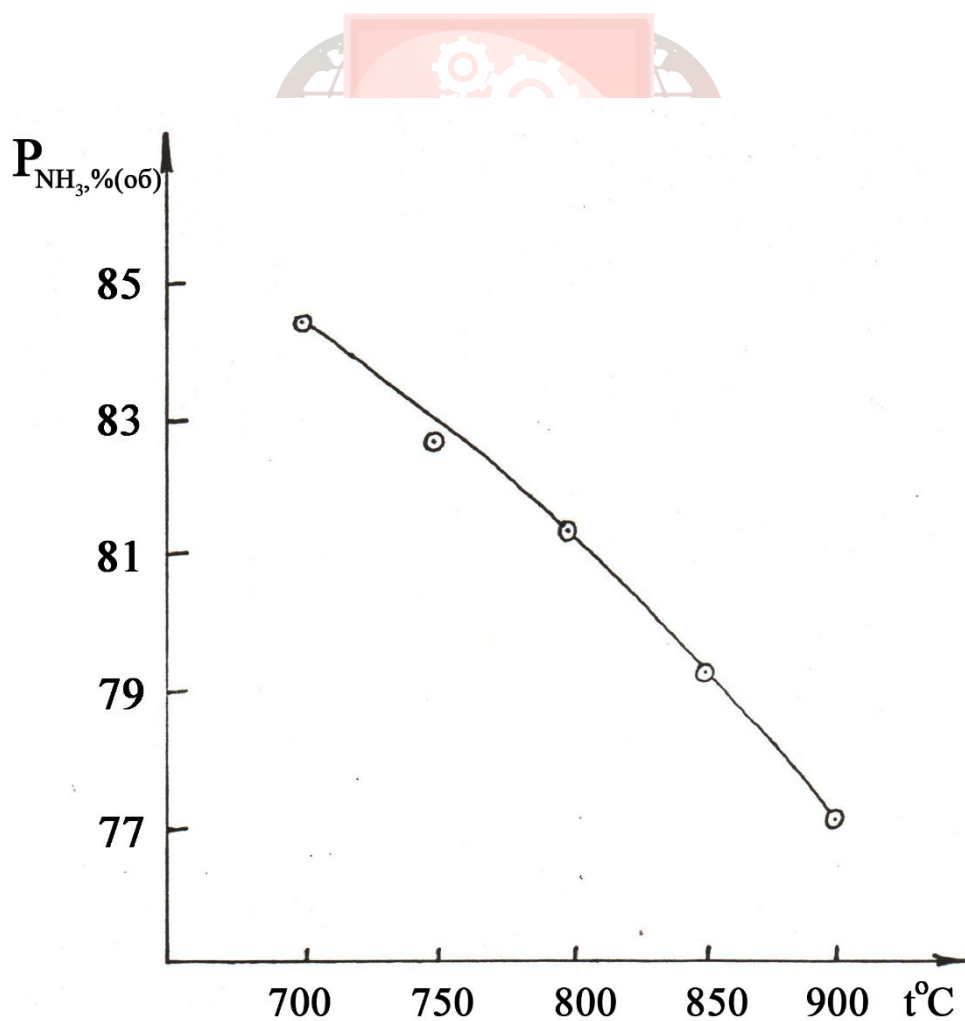


Fig 3. The dependence of the content of carbon dioxide in the exhaust gas from the temperature

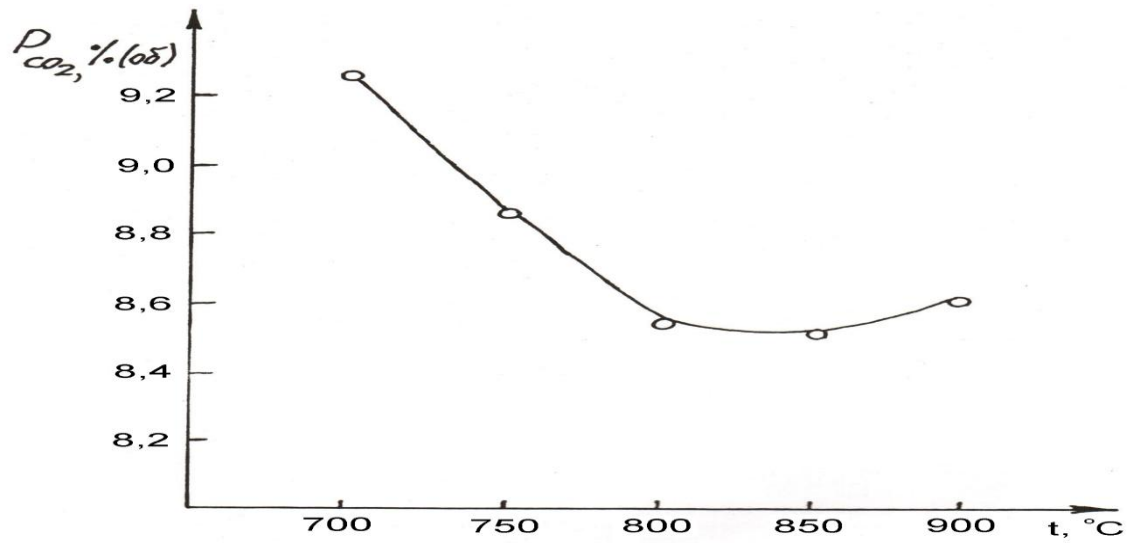


Fig 4. Dependence of the nitrogen content in the exhaust gas on temperature

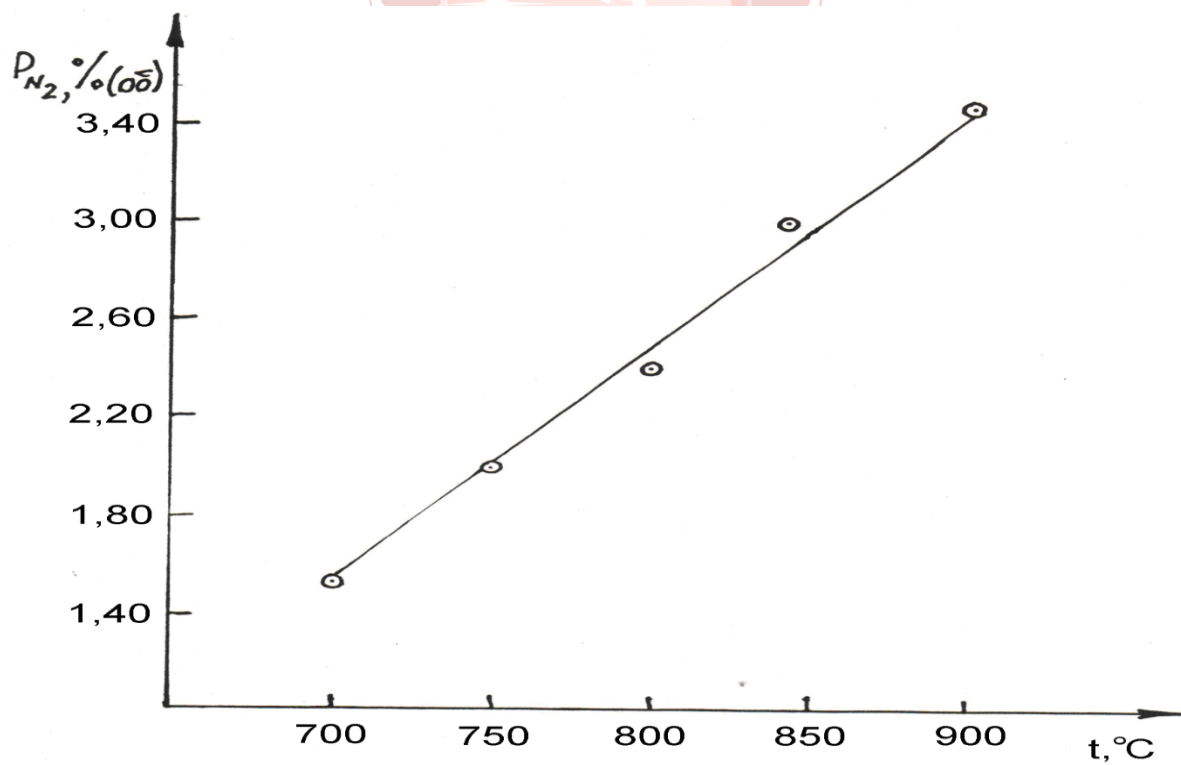


Fig. 5. Dependence of the hydrogen content in the exhaust gases on temperature.

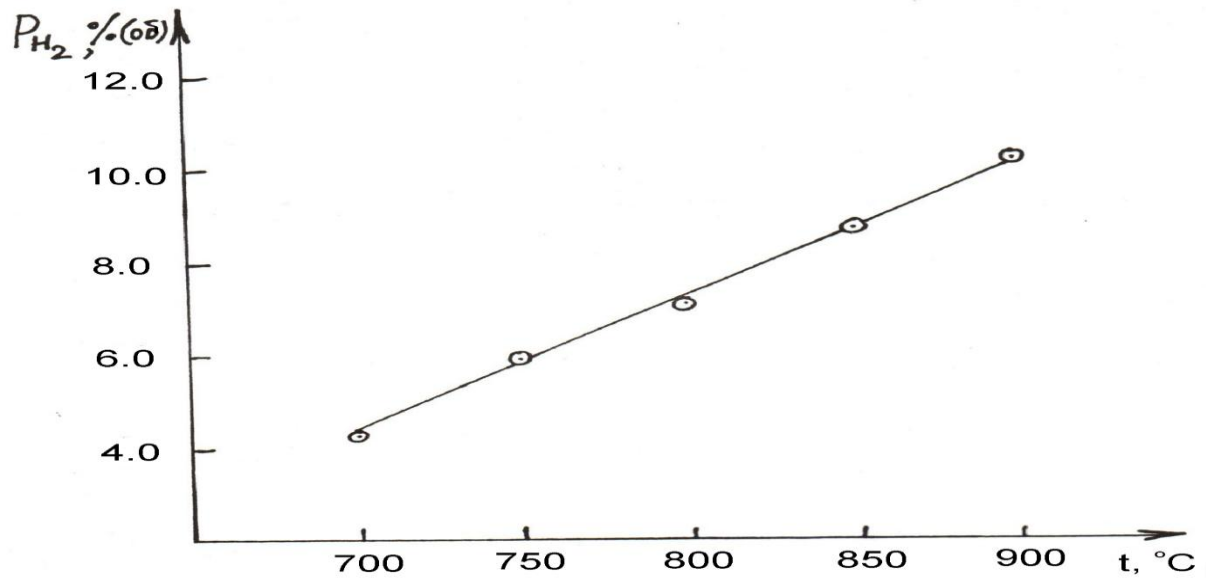


Figure 6. Temperature dependence of carbon monoxide in the exhaust gas.

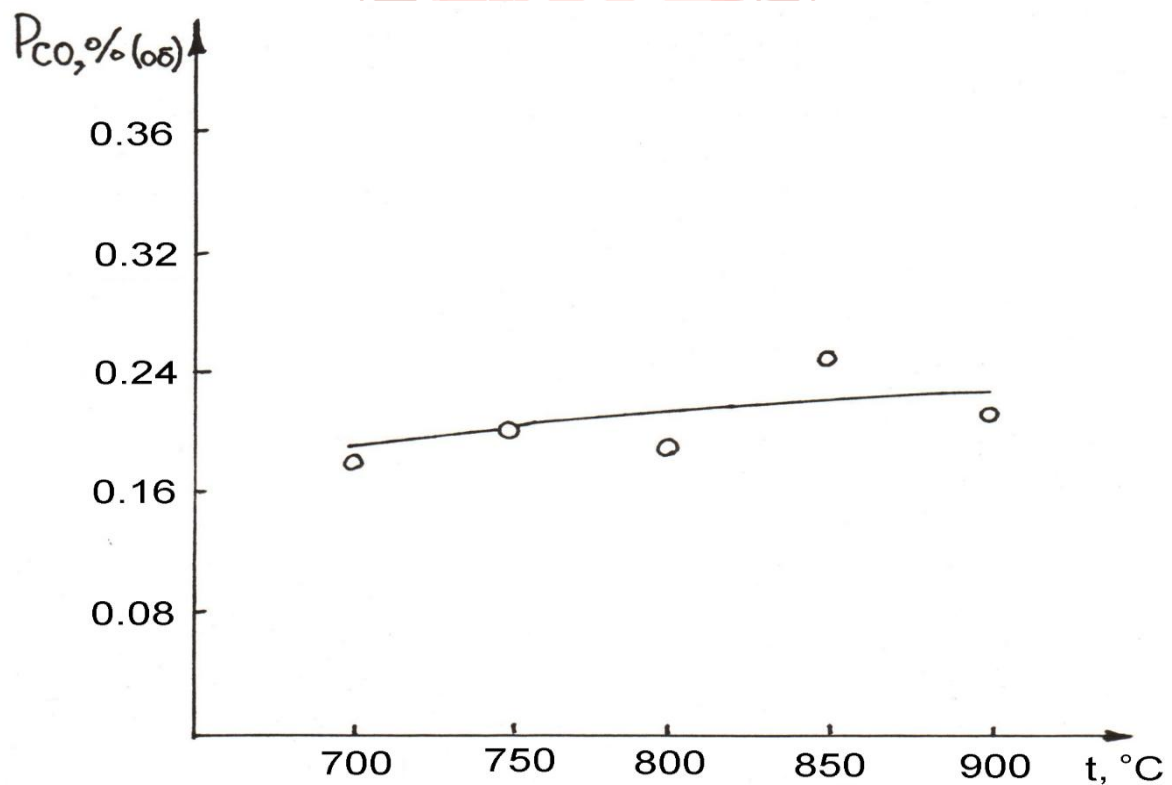
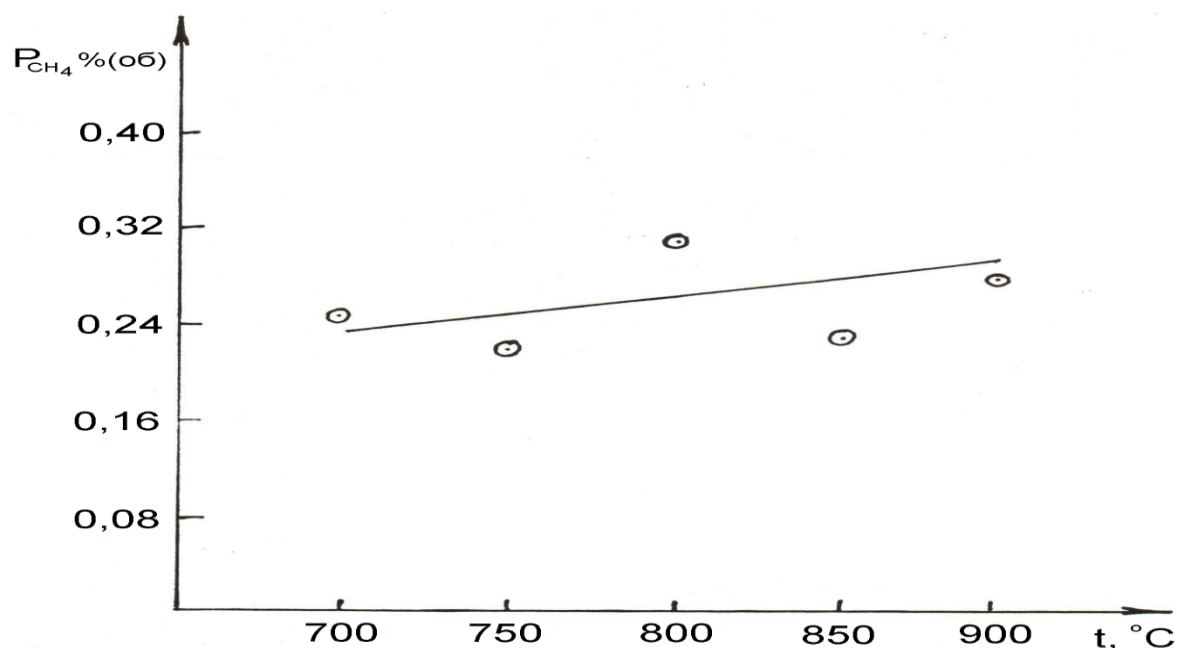


Fig. 7. Dependence of methane content in exhaust gases on temperature.



In this regard, we can conclude that carbon monoxide and methane can be impurities contained in very small quantities in the composition of gas mixtures used for the synthesis of calcium cyanamide, and not as side reaction products $\text{CO}_2 + 2\text{NH}_3 = \text{CH}_4 + \text{H}_2\text{O} + \text{N}_2 + 0.5\text{O}_2$, on the thermodynamic improbability of which was shown in the third chapter.

Fig. 3 show that with an increase in the temperature of the synthesis of calcium cyanamide from 700 to 800 ° C, the carbon dioxide content in the exhaust gases decreases. With a further increase in temperature over 800 ° C, the carbon dioxide content begins to increase.

This circumstance can be explained by the nitrogen content in the product, which first increases and then decreases with increasing temperature. A decrease in the amount of nitrogen in the product leads to the fact that carbon dioxide in a smaller amount enters the chemical reaction of the formation of calcium cyanamide.

Experimental studies on the effect of temperature on the synthesis of calcium cyanamide show that with increasing temperature, the nitrogen content in the product increases, reaching a maximum at 800 ° C, and a further increase in temperature reduces the nitrogen content.

The receipt of a white product in all the experiments proves the absence of free carbon in it.

The product was obtained in the form of solid granules and the nitrogen content in it at an optimum temperature of 800 ° C was 30.2%, which is almost 1.5 times more than in calcium cyanamide obtained by the carbide method.

An analysis of the composition of the gases leaving the reactor showed that with an increase in the synthesis temperature, the content of ammonia and carbon dioxide decreases, and the content of ammonia decreases much more than carbon dioxide, which is explained by the side process of ammonia fixation.

The contents of carbon monoxide and methane in the exhaust gases are minimal [ranges from 0.19 to 0.31% (vol)], which allows us not to consider carbon monoxide and methane as products of any side reactions.

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