

# The Expander Gas and Ammonia Ratio Influence on the Calcium Cyanamide Yield

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## ABSTRACT

For the first time, thermodynamic calculations based on relatively new physicochemical constants clarified the onset temperature of thermal ammonia decomposition, as well as the side chemical reactions probability between ammonia and carbon dioxide. The influence of the main technological parameters on the calcium cyanamide synthesis is investigated. The exhaust gases composition from the reactor for the calcium cyanamide synthesis was studied depending on the temperature. Kinetic studies of the calcium cyanamide synthesis determined the chemical reaction orders with respect to ammonia and carbon dioxide, and it was proved that the limiting stage of calcium cyanamide synthesis is the initial gas components diffusion through the product layer.

**KEYWORDS:** Carbon monoxide, ammonia, expander gas, calcium cyanamide, waste gases

On the basis of long-term physiological and biochemical studies, it has been established that, under salinity conditions, its growth and development or death suppression is the disturbance result in the cells ultrastructure and metabolism and is associated with the equilibrium state disorder of various cations and anions in them. Together with the excessive intake and large amounts of sodium, magnesium, silicon, iron, chlorine and sulfate accumulation in the organs of plants, the calcium intake in them sharply decreases. Cotton belongs to the calciphilic (calcium-loving) plants group and this element plays a special role in its life. Therefore, the physiological calcium deficiency arising during salinization is considered as one of the most important factors limiting the salt tolerance (growth and development) of cotton [1]. Therefore, the mineral fertilizers production development based on our own raw materials, especially calcium containing new mineral fertilizers types, such as calcium cyanamide and others, are becoming important for growing cotton in saline soils and limited water resources.

One of the positive qualities of calcium cyanamide is a more efficient nitrogen absorption by plants from it, because it is a slow acting fertilizer. So, for example, the calcium cyanamide solubility in water is 70 times less than that ammonium nitrate.

Also, unlike ammonium nitrate, calcium cyanamide is an explosion-proof fertilizer.

When applied under fall plowing, it is preferable to all other nitrogen fertilizers forms. In addition to the fertilizing effect, its sterilizing effect on the harmful soil microflora was revealed.

Industrial processing of calcium cyanamide also provides a number of valuable products for various industries, including the gold mining industry.

However, such fertilizers production as calcium cyanamide has not been established in our Republic, and this issue remains relevant to this day.

Based on the above, there is an objective need to activate creating processes of the effective explosion-proof calcium-containing nitrogen fertilizers production based on our own raw materials. Calcium cyanamide, which consists of 50% calcium and may contain up to 34.98% bound nitrogen in amide form, can be considered such a fertilizer. Raw materials for the calcium cyanamide production can be: natural limestone of Uzbekistan, ammonia produced in huge quantities in our Republic, and carbon dioxide, which is an industrial waste of the natural gas conversion process and is emitted into the atmosphere by millions of cubic meters.

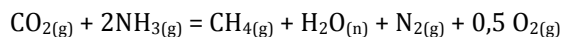
The enterprises of our Republic producing nitrogen fertilizers annually emit million tons of gas into the atmosphere, containing carbon dioxide and other gases. These waste gases are called **expansive** gases. In the calcium cyanamide synthesis, a clean or "dirty" expander gas fraction was used. The pure expander gas fraction had the composition: CO<sub>2</sub> – 99,90%, H<sub>2</sub> – 0,02%, N<sub>2</sub>+Ar – 0,01%, monoethanolamine – 5mg/m<sup>3</sup>, H<sub>2</sub>S – 1mg/m<sup>3</sup>, the "dirty" fraction composition: CO<sub>2</sub> – 95,00%, H<sub>2</sub> – 4,50%, monoethanolamine – 5mg/m<sup>3</sup>, H<sub>2</sub>S – 1mg/m<sup>3</sup>. During the calcium cyanamide synthesis by the action of an ammonia and carbon dioxide gas mixture on calcium oxide, it is important to study the loss issue of a relatively expensive starting component - ammonia due to thermal decomposition and side reaction of the ammonia and carbon dioxide interaction [2].

The calculation equation, according to Gibbs energy definition, of the thermal ammonia decomposition process into elemental nitrogen and hydrogen according to the NH<sub>3(g)</sub> = 0,5 N<sub>2(g)</sub> + 1,5 H<sub>2(g)</sub> reaction, compiled in 1974 on the basis of physicochemical constants 1947-1972 can be considered obsolete, since over the next ten years, they were revised and refined by a number of authors.

In this regard, we performed a number of thermodynamic calculations based on relatively new physicochemical constants to solve the following problems:

- the average relative error determination in the thermodynamic calculations results using the old and new change constants in enthalpy, equilibrium constant and Gibbs energy in the temperature range 373-1473°K with 100°K step for the thermal ammonia decomposition process;
- determination of a new temperature value of the thermodynamic ammonia probability beginning decomposition process;

- thermodynamic determination of the ammonia losses possibility due to chemical interaction, in the temperature range 673-1473°K with 100°K step, of the initial gas components - ammonia and carbon dioxide by the following reaction:



To perform thermodynamic calculations, Table 1 shows new physicochemical constants values.

**Table 1 Thermodynamic components constants**

№ п/п	Substance and its aggregation state	$\Delta H^{\circ}_{238}$ , kcal/mol	$S^{\circ}_{238}$ , cal/mol. temp	Equation coefficients				Temperature range, K
				$C^{\circ}_p=f(T)$				
				$C^{\circ}_p=a+b*T+cT^2$				
$C^{\circ}_p= a+b*T+c^1/T^2$				a	b*10 <sup>3</sup>	c <sup>1</sup> *10 <sup>-5</sup>	c*10 <sup>6</sup>	
1	2	3	4	5	6	7	8	9
1.	NH <sub>3(g)</sub>	-10,980	46,047	7,122	6,090	-0,399	-	298-1800
2.	N <sub>2(g)</sub>	0	45,770	6,663	1,021	-	-	298-2500
3.	H <sub>2(g)</sub>	0	31,195	6,520	0,779	0,119	-	298-3000
4.	CO <sub>2(g)</sub>	-94,051	51,066	10,550	2,161	-2,041	-	298-2500
5.	CH <sub>4(g)</sub>	-17,890	44,520	3,4243	17,844	-	-	298-1500
6.	H <sub>2O(l)</sub>	-57,7944	45,105	7,170	2,560	0,079	-	298-2500
7.	O <sub>2(g)</sub>	0	49,006	7,519	0,810	-0,901	-	298-3000

In this table:

$\Delta H^{\circ}_{238}$  – change in enthalpy as a result of the reaction of one mole of a given compound (substance) from simple substances under standard conditions.

$S^{\circ}_{238}$  – absolute value of entropy of a compound (substance) under standard conditions

$C^{\circ}_p$  – the true molar isobaric heat capacity of the compound (substance) at P = 101.325 kPa (1 atm) and the temperature T degrees Kelvin, different from 298K.

a,b and c<sup>1</sup> - constants for a given inorganic substance, the equation coefficients for calculating the true molar isobaric heat capacity at different temperatures T and pressure P =101,325 kPa (1 atm).

a,b,c – constants for a given organic matter, the equation coefficients for calculating the true molar isobaric heat capacity at different temperatures T and pressure P=101,325 kPa (1 atm).

Thermodynamic quantities values  $\Delta H^{\circ}_{238}$  and  $S^{\circ}_{238}$  are given for standard conditions: pressure P=101,325 kPa (1 atm) and T=298 K.

In earlier studies continuation [1,2] on the calcium cyanamide synthesis from lime mixture, the used reaction gas mixture consisted of carbon dioxide and ammonia.

When conducting experimental studies, the CO<sub>2</sub>:NH<sub>3</sub> ratio was changed in the range from 12: 1 to 1:12 (table).

Ratio CO <sub>2</sub> :NH <sub>3</sub>	12:1	9:1	5:1	3:1	1:1	1:3	1:5	1:9	1:12
Nitrogen content in the product, %	26,76	25,90	25,08	25,69	25,90	28,65	29,38	31,27	31,34

The presented data show that the ammonia content in the initial gas mixture has a greater effect than the carbon dioxide content. For example, an increase in the CO<sub>2</sub>:NH<sub>3</sub> ratio from 1: 1 to 12: 1 increases the nitrogen content in the product from 25.9 to 26.76, and with a 1: 9 ratio, from 25.9 to 31.27%, i.e. by 5.37%.

With an increase in the ratio CO<sub>2</sub>:NH<sub>3</sub> over 1: 9, the nitrogen content in the product practically does not increase, which allows us to consider the optimal CO<sub>2</sub>:NH<sub>3</sub>=1:9.

For the calcium cyanamide synthesis, the interaction time of the initial gas mixture with lime is a very important factor, since this determines both the gas mixture flow rate and the installation productivity.

In further experiments, the passage duration of the gas mixture through the charge was varied in the range of 15-120 minutes.

The obtained data showed, as we expected that with an increase in the effect duration of the gas mixture on the solid phase, the nitrogen content in the product increases and the nitrogen content dependence in the product on time largely correspond to equilibrium processes.

The process driving force, which is determined by what difference between the partial and equilibrium pressures ( $\Delta P = P_{\text{partial}} - P_{\text{equ}}$ ) is more important in the initial period, when the system is still far from equilibrium. As equilibrium is approached, the  $\Delta P$  driving force decreases, which cause a decrease in the rate of nitrogen accumulation in the product. At the moment of reaching equilibrium ( $\Delta P = 0$ ), the nitrogen amount in the product reaches its maximum (equilibrium) value.

This confirms the nature of the experimental data, in which, in the initial period (up to 90 minutes), the nitrogen content practically increases in a straight line, and then tends to constancy.

The above experiments series allow us to conclude that for the calcium cyanamide synthesis by a gas mixture action of carbon dioxide and ammonia on lime, the optimal ratio of carbon dioxide to ammonia is 1: 9, and the optimal time of chemical components interaction is 90 minutes.

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