

The Calculus of the Operation Parameters at Pressure of the Primary Separation Column of the ^{15}N Production Plant

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The relations for calculus of: 10M HNO₃ solution flow, isotopic transport, ^{15}N molar fraction at the bottom of the separation column, product flow, interphasic transfer velocity, height equivalent to the theoretical plate and sulfur dioxide flows in both stages of the product refluxer are presented for ^{15}N separation column with different diameters and 10M HNO₃ feeding flow rates, operated at pressure up to 1.5 atm. In order to produce the isotope ^{15}N at 99 at. % ^{15}N by isotopic exchange in Nitrox system it is desirable to operate the production plant at biggest flow of 10M HNO₃ solution, which allows the ^{15}N production at that concentration on a given plant. That will be possible by operating the plant at pressure as it is shown in this work. At 0.8 atm pressure (1.8 atm absolute) the isotopic separation at higher flow rates would be practically equal with that obtained at lower flow rates and atmospheric pressure. For constant: HETP = 10.85 cm, ^{15}N molar fraction of the feeding 10M HNO₃, $N_f = 0.00365$, and of the product, $N_p = 0.12$, the variation of the primary separation column product and of the ^{15}N production plant, as a function of the feeding flow with 10M HNO₃ solution, are also presented.

Keywords: ^{15}N production, Nitrox system, operation parameters at pressure

The most utilized method for ^{15}N production is based on the $^{15}\text{N}/^{14}\text{N}$ exchange in (NO, NO₂)_(g) - HNO_{3(s)} system (Nitrox). At National Institute for R and D of Isotopic and Molecular Technologies, Cluj-Napoca, Romania, [1] ^{15}N is produced at 99 at. % ^{15}N concentration by above mentioned methods, this Institute being the single producer of ^{15}N in EU.

It was experimentally proved on a laboratory scale plant that at 0.8 atm (1.8 atm absolute) it is possible to increase the flow rate of 10M HNO₃ in the ^{15}N separation column 1.57 times in comparison with the operation at atmospheric pressure [2].

The goal of this work is to calculate the operation parameters at different pressures up to 1.5 atm: the flow rate of 10M HNO₃, the isotopic transport, the ^{15}N concentration, the maximum product flow, the interphase transfer velocity and HETP, that would be utilized in the primary separation column of ^{15}N production plant. It will be also calculate the sulfur dioxide flow in the product refluxer of the primary separation column.

The primary separation column of the ^{15}N production plant [1] has the following characteristics: length (Z) = 733 cm; packing: stainless steel triangular wire springs 2.3 x 2.3 x 0.2 mm; inside diameter: 80 mm; the cross section area: 50.26 cm².

Expression of the ^{15}N transport at total reflux

Considering the material balance, the maximum product of separation column, or the ^{15}N transport between the both participants to the isotopic exchange in the column: the gaseous mixture of the nitrogen oxides (NO, NO₂) and 10M HNO₃ solution (liquid phase) is:

$$PN_p = T = [L_f N_f (\alpha - 1)(1 - N_p) + PN_f] / [1 + (\alpha - 1)(1 - N_p)] \quad (1)$$

where: P is the product flow, (M/h); N_p is the ^{15}N molar fraction in the product; N_f is the ^{15}N molar fraction in the 10M HNO₃ feeding the primary separation column, 0.00365; T is the transport of ^{15}N between both participants to the isotopic exchange (M/h); α is the single stage

separation factor, 1.055 at 25°C. At small ^{15}N concentration to the feeding point of the separation column we have:

$$PN_p \sim T \sim L_f N_f (\alpha - 1)(1 - N_p) \quad (2)$$

It will be introduced the specific flow, or flow rate I, which is the ratio between the 10M HNO₃ solution flow in the primary separation column and the cross section area (mL/cm².min).

The 10M HNO₃ solution flow in the separation column, L_f , expressed in term of the nitric acid flow rate, I, and cross section area (s) is:

$$L_f = 0.6 \cdot s \cdot I, \quad (\text{M/h}) \quad (3)$$

Considering the above mentioned values of N_f and α and equations (2, 3) results the general expression of the transport, applicable to any ^{15}N separation column, using the $^{15}\text{N}/^{14}\text{N}$ exchange in Nitrox system:

$$T = 1.2 \times 10^{-4} \cdot s \cdot I, \quad (\text{M/h}) \quad (4)$$

The isotopic concentration at the bottom of the separation column

The total isotopic separation at steady state and total reflux is:

$$S = N_b / (1 - N_b) / N_f / (1 - N_f) \quad (5)$$

where: N_b and N_f are the ^{15}N molar fractions in nitric acid or nitrogen oxides, measured at the bottom and in the top of the separation column; n is the number of the transfer unities, or theoretical plates, achieved in the separation column:

$$n = Z/\text{HETP} \quad (6)$$

where: HETP is the height equivalent to the theoretical plate (cm).

Initially is measured ^{15}N molar fraction on nitrogen oxides samples from the bottom and in the top of the separation column, at steady state and total reflux, then

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the total isotopic separation and the number of transfer unities (n) are calculated, [2]. In the same operation conditions can be calculated the ^{15}N molar fraction at the column bottom, if HETP (for the specific packing and 10M HNO_3 flow rate) and the column length (Z) are known, by using the following relation:

$$N_b = 3.66 \times 10^{-3} \times 1.055^{Z/\text{HETP}} / (1 + 3.66 \times 10^{-3} \cdot 1.055^{Z/\text{HETP}}) \quad (7)$$

The maximum product of a separation column (plant)

The maximum product flow of a ^{15}N separation column (plant) [4] is given by:

$$P = L_f N_f (1 - N_p) (\alpha - 1) / \{ N_p [1 + (1 - N_p) (\alpha - 1)] - N_p \} \quad (8)$$

and, by introducing the following values: $\alpha = 1.055$; $N_f = 0.00365$; $N_p = 0.99$, the equation will change to:

$$P = 1.15 \cdot 10^{-4} \cdot s \cdot I \quad (\text{M/h}) \quad (9)$$

The interphasic transfer velocity and HETP

In a simplified mathematical model it would be considered only the isotopic global $^{15}\text{N}/^{14}\text{N}$ exchange between the chemical compounds of the gaseous phase and those of the liquid one at total reflux. If Γ is the specific flow of the 10M HNO_3 solution, the same as the specific flow of the gas, the mass transfer equations in a separation column will be reduced to only one:

$$\Gamma \, dY/dz = k(\alpha - 1)X \quad (10)$$

where: Γ is the specific flow of 10M HNO_3 solution ($\text{M}/\text{cm}^2 \cdot \text{s}$); X is the ^{15}N molar fraction in the chemical compounds of the gaseous phase; Y is the ^{15}N molar fraction in the chemical compounds of the liquid phase (10M HNO_3 solution); k is the interphasic transfer velocity referring to the packed separation column volume ($\text{M}/\text{cm}^3 \cdot \text{s}$); z is the height of the separation column considered from the top to the bottom (cm).

The solution of equation (10) is:

$$Y(z) = Y(o) \cdot e^{k(\alpha - 1)z/\Gamma} \quad (11)$$

$Y(o)$ being the ^{15}N molar fraction in the feeding: 10M HNO_3 solution

$$(Y(o) = N_p).$$

When is available experimentally measured values of the ^{15}N molar fraction at the column bottom, $Y(z)$, the ^{15}N separation at steady state would be calculated with a relation similar to (5):

$$S_n = Y(z)/(1 - Y(z))/Y(o)/(1 - Y(o)) \quad (12)$$

which can be reduced to:

$$S_n \sim Y(z)/Y(o) \quad (13)$$

for $Y(z) < 0.1$ (for instance in the case of the primary separation column of the ^{15}N production plant). From equation (11) and (12) the expression of the interphasic transfer velocity is obtained:

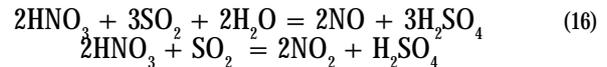
$$k = \Gamma \cdot \ln S_n / Z(\alpha - 1) \quad (\text{M}/\text{cm}^3 \cdot \text{s}) \quad (14)$$

and from equations (5, 6) the expression of HETP is:

$$\text{HETP} = \Gamma \cdot \ln \alpha / k(\alpha - 1) \quad (\text{cm}) \quad (15)$$

The sulfur dioxide consumption in the product refluxer of the primary separation column

At the bottom of the primary separation column nitric acid is totally converted into nitrogen oxides by reaction with sulfur dioxide. In the first stage of the refluxer the following reactions take place:



and, in the second stage of the refluxer, the nitrogen dioxide is reduced to nitric oxide by reaction with an additional sulfur dioxide quantity:



The nitric oxide (gas) is introduced at the bottom of the primary separation column, providing the reflux at this point of the ^{15}N separation plant.

If the primary separation column is fed with 60 M/h HNO_3 , respectively 6 L/h 10M HNO_3 solution, it was experimentally measured a SO_2 feeding flow of 450 L/h (NTP) or 18.75 M/h, in the second stage of the product refluxer. It means that in the first stage of the refluxer is produced 18.75 M/h nitrogen dioxide and 41.25 M/h nitric oxide (16). For nitric oxide production the consumption of SO_2 is 61.875 M/h (1485 L/h) and for 18.75 M/h NO_2 the SO_2 consumption is 9.375 M/h (225 L/h) in the first stage of the product refluxer. For nitric oxide production the SO_2 consumption is 61.875 M/h (1485 L/h) and for 18.75 M/h NO_2 the SO_2 consumption is 9.375 M/h (225 L/h) in the first stage of the product refluxer. In both stages of the product refluxer the sulfur dioxide consumption is $1710 + 450 = 2160$ L/h, or 90 M/h. It can be calculated, for any product refluxer of the same type, by using the relation:

$$\text{SO}_2 \text{ Flow} = 0.9 \cdot s \cdot I, \quad (\text{M/h}) \quad (18)$$

where: s is the cross section area of the separation column, (cm^2) and I is the specific flow of 10M HNO_3 solution in the primary column ($\text{mL}/\text{cm}^2 \cdot \text{min}$). The SO_2 flow in the first stage of the refluxer is 78.76% of total flow (18), namely: $0.709 \cdot s \cdot I$, (M/h) and in the second stage: $0.191 \cdot s \cdot I$, (M/h).

The $Y(z)$ (in at. % ^{15}N) and S_n experimentally determined for primary separation column [1], together with calculated values of the interphasic transfer velocity, k (14), HETP (15) for $I = 2 \text{ mL}/\text{cm}^2 \cdot \text{min}$ and atmospheric pressure, and SO_2 flows in both stages of the product refluxer are presented in table 1.

$Y(z)$, table 1, were measured at the bottom of the primary separation column at steady state and total reflux. The first two values of $Y(z)$, (table 1) were obtained when a single stage product refluxer was utilized, [1], and the suitable ratio between NO and NO_2 concentrations, in the gaseous mixture refluxed at the bottom of the primary separation column, was obtained by adding water in the product refluxer, (16), [1].

Results and discussions

The data obtained on an experimental separation column 100 cm length and 18 mm inside diameter, with the same type of packing as of the primary separation column, are presented in the table 2, [2].

At atmospheric pressure and 10M HNO_3 flow rate of $2.49 \text{ mL}/\text{cm}^2 \cdot \text{min}$ HETP increased with 25% in comparison with its value at $1.57 \text{ mL}/\text{cm}^2 \cdot \text{min}$. At the same pressure and $2.36 \text{ mL}/\text{cm}^2 \cdot \text{min}$ flow rate HETP decreased with 7%

in comparison with its value at atmospheric pressure and 1.5 times smaller flow rate. At 0.8 atm and 3.14 mL/cm² · min HETP is practically equal to the value at atmospheric pressure and at two times smaller 10M HNO₃ flow rate. At a pressure of 1.5 atm and 3.93 mL/cm² · min 10M HNO₃ HETP increased with 26% in comparison with its value at 0.8 atm and 3.14 mL/cm² · min flow rate.

It should be mentioned that our kinetic data showed that the rate of the ¹⁵N/¹⁴N exchange in NO_(g) - HNO_{3(s)} system linearly depends on the nitric oxide pressure, the reaction rate equation being:

$$R = k[\text{HNO}_3][\text{N}_2\text{O}_3] \quad (19)$$

where [HNO₃] and [N₂O₃] are the nitric acid and dinitrogen trioxide concentrations in the liquid phase (nitric acid solution), [N₂O₃] being proportional with the pressure of gaseous nitric oxide [6, 7].

From the data of table 2 it is clear that the velocity of the isotopic transfer between the two phases in contact depends on the flow rate of the 10M HNO₃ solution in the separation column (I) and it has a convenient value for I = 3.14 mL/cm² · min. At that flow rate, feasible for a pressure of 0.8 atm in the separation column, the HETP is also convenient, providing the same ¹⁵N separation as in the operation at atmospheric pressure.

One more reason for increasing the flow rate of 10M HNO₃ solution in the primary separation column is the value of the interphasic ¹⁵N transport, calculated with equation (4): T₂ = 1.206 · 10⁻² M/h, for I = 2 mL/cm² · min and atmospheric pressure, respectively T_{3.14} = 1.89 · 10⁻² M/h, for I = 3.14 mL/cm² · min and 0.8 atm.

In accordance with experimental data presented in table 2, the operation of the primary separation column of

the production plant at a flow rate of 3.14 mL/cm² · min and 0.8 atm pressure will not modify the ¹⁵N separation. The difference between HETP obtained for 1.57 mL/cm² · min and for 3.14 mL/cm² · min is not important showing the possibility to use a feeding of 95 M/h 10M HNO₃ at 0.8 atm pressure, instead of 60 M/h at atmospheric pressure.

The ratio between HETP = 4.72 cm, measured on the final separation column of the ¹⁵N production plant [1] at a flow rate of 1.77 mL/cm² · min and atmospheric pressure and HETP = 4.17 cm, obtained on the experimental separation column at a flow rate of 3.14 mL/cm² · min and 0.8 atm pressure (table 2) is 1.13. Considering that HETP for primary separation column will decrease in the same measure for a flow rate of 3.14 mL/cm² · min and 0.8 atm pressure, it arrives at a HETP = 9.60 cm, instead of 10.85, determined at atmospheric pressure. By using that HETP and equation (7), the ¹⁵N concentration, which could be obtained at the bottom of the primary separation column, is N_b = 0.179, or 17.9 at. % ¹⁵N. If the HETP remains at 3.14 mL/cm² · min flow rate and 0.8 atm pressure, the same as the HETP at 2 mL/cm² · min and atmospheric pressure, the ¹⁵N concentration at the column bottom would be N_b = 0.12, or 12 at. % ¹⁵N (table 3).

The ratio between HETP = 4.72 cm, measured on the final separation column [1] in the above mentioned conditions and HETP = 3.85 cm, measured on the experimental column at flow rate of 2.36 mL/cm² · min and 0.5 atm pressure (table 2) is 1.226. Considering that HETP, for primary separation column, will decrease in the same measure at 2.36 mL/cm² · min flow rate and 0.5 atm pressure, it arrives at HETP = 8.85 cm. With that value it could be obtained N_b = 0.2986, or 29.86 at. % ¹⁵N.

The ratio between HETP = 4.72 cm (on the final separation column) and HETP = 5.27 cm (on the experimental column, for I = 3.93 mL/cm² · min at 1.5

Table 1
THE ¹⁵N CONCENTRATION AT THE BOTTOM OF THE SEPARATION COLUMN, ISOTOPIC SEPARATION AND OTHER PARAMETERS FOR I = 2 mL/cm² · min AND ATMOSPHERIC PRESSURE

Y(z) (at % ¹⁵ N)	S _∞ (12)	k · 10 ³ (M/cm ³ · sec)	HETP (cm)	SO ₂ flow First stage (M/h)	SO ₂ flow First stage (M/h)
3.62	10.25	1.91	16.86	71.77	-
5.60	16.19	2.29	14.10	71.77	-
9.00	27.00	2.71	11.91	71.77	18.69
12.00	37.00	2.97	10.85	71.77	18.69

Table 2
THE ¹⁵N CONCENTRATIONS AT THE BOTTOM OF THE EXPERIMENTAL SEPARATION COLUMN, ¹⁵N SEPARATION AT STEADY STATE AND OTHER PARAMETERS FOR OPERATION AT DIFFERENT PRESSURES

10M HNO ₃ (ml/h)	I (ml/cm ² · min)	Y(z) (at % ¹⁵ N)	S _∞ (13)	k · 10 ³ (M/cm ³ · sec)	HETP (cm)	Pressure (atm)
240	1.57	1.338	3.665	6.187	4.12	atm
380	2.49	1.024	2.80	7.769	5.2	atm
480	3.14	0.919	2.52	8.794	5.79	atm
360	2.36	1.470	4.02	9.949	3.85	0.5
480	3.14	1.320	3.61	12.20	4.175	0.8
600	3.93	1.007	2.76	12.21	5.27	1.5

Table 3
CALCULATED DATA FOR DIFFERENT FLOWS (FLOWS RATES) IN THE PRIMARY SEPARATION COLUMN.

10M HNO ₃ (ml/h)	I (ml/cm ² ·min)	Pressure (atm)	HETP (cm)	S (5)	N _t	N _b	n
6000	2	atm	10.85	37.22	0.00365	0.120	67.74
7118	2.36	0.5	8.85	116.2	0.00365	0.298	88.82
9468	3.14	0.8	9.60	59.60	0.00365	0.179	76.35
9468	3.14	0.8	10.85	37.22	0.00365	0.120	67.74
11851	3.93	1.5	12.11	25.55	0.00365	0.0855	60.52

10M HNO ₃ (ml/h)	I (ml/cm ² ·min)	Pressure (atm)	P · 10 (M/h)	HETP (cm)	P · N _b · 10 ²
6000	2	atm	0.976	10.85	1.172
7118	2.36	0.5	0.458	8.85	1.365
9468	3.14	0.8	1.023	9.60	1.831
9468	3.14	0.8	1.540	10.85	1.848
11851	3.93	1.5	2.756	12.11	2.342

Table 4
THE MAXIMUM PRODUCT OF THE PRIMARY SEPARATION COLUMN OPERATED AT DIFFERENT PRESSURES

10M HNO ₃ (ml/h)	I (ml/cm ² ·min)	P(8) · 10 (M/h)	P(8) · N _b · 10 ²	P(9) · 10 ² (M/h)
6000	2	0.976	1.171	1.159
7000	2.32	1.139	1.367	1.345
8000	2.65	1.300	1.560	1.536
9000	2.98	1.464	1.757	1.727
9468	3.14	1.540	1.848	1.820
10000	3.31	1.627	1.952	1.918
11000	3.65	1.790	2.148	2.115
12000	3.98	1.950	2.340	2.307

Table 5
THE PRODUCT OF THE PRIMARY SEPARATION COLUMN AND OF THE ¹⁵N PRODUCTION PLANT AS A FUNCTION OF 10M HNO₃ FEEDING FLOW

atm, table 2) is 0.8956. Considering that HETP for primary separation column will increase in the same measure, it arrives at HETP = 12.11 cm, and N_b = 0.0855, or 8.55 at. % ¹⁵N, (table 3).

It was also calculated the maximum product (8) of the primary separation column, operated at different pressure and flow rates (table 4).

For constant HETP = 10.85 cm, N_t = 0.00365 and N_b = 0.12, the variation of the primary separation column product P (8), as a function of feeding flow with 10M HNO₃ solution, is presented in table 5. The product of ¹⁵N production plant [1] is also presented for N_t = 0.00365 and N_b = 0.99 (99 at. % ¹⁵N) and different 10M HNO₃ solution flows.

At flow rates higher than 3.14 mL/cm² · min 10M HNO₃ solution HETP increases and therefore will decrease the isotopic separation; the ¹⁵N molar fraction, which can be reached at the bottom of the primary separation column, would be 0.0855 compared to 0.12, which is taken as reference.

Conclusions

The achieved relations for calculus of: 10 M HNO₃ solution flow, isotopic transport, ¹⁵N molar fraction at the

bottom of the separation column, product flow, interphasic transfer velocity, height equivalent to the theoretical plate and sulfur dioxide flows in the both stages of the product refluxer, allow obtaining of those parameters for ¹⁵N separation columns with different inside diameters and 10M HNO₃ feeding flow rates.

In order to produce the isotope ¹⁵N at 99 at. % ¹⁵N it is desirable to operate the production plant at the biggest flow of 10M HNO₃ solution, which allows the ¹⁵N production at desired concentration on a given plant. That will be possible by operating the plant at pressure as it is shown in this work. It is true that at higher flow rates of 10M HNO₃ solution the increasing of HETP can become excessive. In spite of that, higher is flow rate, shorter will be the time to reach the steady state and higher the isotopic transport between the two phases.

At 0.8 atm pressure (1.8 atm absolute) the isotopic separation at higher flow rates would be practically equal to that obtained at lower flow rates at atmospheric pressure. The efficiency increasing of the ¹⁵N separation at pressure can be explained if it is taken into consideration that ¹⁵N/¹⁴N exchange rate in the nitrogen oxides - nitric acid system increases with pressure.

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