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PRODUCTION OF ^{15}N-ENRICHED NITRIC ACID ($H^{15}NO_3$)

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Abstract - Techniques that employ ^{15}N have proved to be an important tool in many areas of the agronomic and biomedical sciences. Nevertheless, their use is limited by methodological difficulties and by the price of compounds in the international market. Nitric compounds ($^{15}NO_3^-$) have attracted the interest of researchers. However, these compounds are not currently produced in Brazil. Thus, in the present work $H^{15}NO_3$ was obtained from the oxidation of anhydrous $^{15}NH_3$. The method we used differs from the industrial process in that the absorption tower is replaced with a polytetrafluoroethylene-lined, stainless-steel hydration reactor. The process output was evaluated based on the following parameters: reaction temperature; ratio of reagents; pressure and flow of $^{15}NH_{3(g)}$ through the catalyst (Pt/Rh). The results showed that, at the best conditions (500 ºC; 50 % excess O_2; 0.4 MPa; and 3.39 $g.min^{-1}$ of $^{15}NH_3$), a conversion percentage (N-$^{15}NH_3$ to N-$^{15}NO_3^-$) of 62.2 %, an overall nitrogen balance (N-$^{15}NH_3$ + N-$^{15}NO_3^-$) of 86.8 %, and purity higher than 99 % could be obtained.

Keywords: Nitric compounds; Catalyst; Reactor; Stable isotope.

INTRODUCTION

Nitrogen is considered to be a limiting factor for primary production, both on land and in the aquatic environment, since it is the main component of enzymes that control the biochemical reactions in which carbon is reduced and oxidized (Schelsinger, 1991). In most studies involving stable isotopes (tracer), isotopes of light elements are used, such as nitrogen and its isotopes, which have great importance in biological systems studies, and also take part in most geochemical reactions (Fritz and Fontes, 1989).

Under natural conditions, nitrogen has two stable isotopes, ^{14}N and ^{15}N, with isotopic abundances of 99.73 and 0.37% in atoms, respectively (Weast, 1998). The existence of the heavy nitrogen isotope (^{15}N) allows the production of compounds enriched in this isotope, characterized by having isotopic abundances above those naturally found. These compounds, in turn, allow the isotopic technique to be used in many research studies, and allow many of the aspects involved in the nitrogen cycle to be elucidated, in both the agronomic (soil-plant-atmosphere system) (Trivelin et al., 2002) and biomedical fields (Dichi et al., 1998).

The isotopic technique that uses ^{15}N as tracer basically consists of supplying the organism under study with a chemical compound in which the isotopic ratio ($^{15}N/^{14}N$) of the compound under consideration is different from that naturally found, and then evaluating the isotope's distribution in the system under study. In many research studies involving the ^{15}N isotopic technique in the

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*To whom correspondence should be addressed agronomic and biomedical fields, nitrogen compounds highly enriched in the isotope have to be used, due to the isotopic dilution of the systems under study (Knowles and Blackburn, 1993). Until recently, these compounds were not produced in Brazil and South America, due to difficulties of a methodological nature. Such compounds had to be imported from the United States, Europe, or Asia at high prices, which varied proportionally depending on enrichment and type of compound. $H^{15}NO_3$ (50% m/v solution) enriched at 95 % in atoms of ^{15}N has a FOB price on the order of U$90.00 (ninety dollars) per gram on the international market.

Consequently, the production of ^{15}N-labeled nitric compounds is being requested by researchers to be used in agronomic investigations, particularly for factors that allow information to be obtained on the nitrogen cycle. Within this context, we could highlight the marked mobility of nitrogen, with emphasis on the occurrence of losses caused by volatilization (loss in gaseous forms), biological immobilization, erosion, and leaching.

The technology of isotopic separation and production of ^{15}N-enriched compounds is not shared by other countries, due to economic or even strategic factors. In this respect, some studies have been developed in Brazil (Maximo et al., 2000; Bendassolli et al., 2002; Bendassolli et al., 1988; Bendassolli et al., 1989; Bendassolli, 1991; Tavares et al., 2006; Maximo et al., 2005; Oliveira, 2000; Tavares, 2005).

From the above, considering the control over the methodology of isotopic separation and the importance of making other ^{15}N-enriched nitrogen compounds available for the country's researchers at lower-than-FOB prices, the objective of this study was the production (in batches) of ^{15}N-enriched $H^{15}NO_3$, and to evaluate the parameters (reaction temperature, ratio between reagents, system pressure and flow of $^{15}NH_{3(g)}$ through the catalyst) involved in the process.

EXPERIMENTS

Gases (O_2, N_2, NH_3) and Isotope (^{15}N)

Oxygen (O_2) 5.0 (99.999 %) and commercial nitrogen (N_2) (97 to 98 %) were used. The tests, aimed at evaluating the parameters involved in the process, were performed using NH_3 (1,8 g) with natural isotopic abundance (0.366 % in atoms of ^{15}N), and purity in the order of 99 % (2.0). Anhydrous $^{15}NH_3$ enriched to 90 % in atoms of ^{15}N (Bendassolli, et al., 2002), was used as an isotopic source for the production of $H^{15}NO_3$.

$H^{15}NO_3$ Production Process

The complete $H^{15}NO_3$ production system is represented schematically in Figure 1, while Figure 2 shows in detail the gas loading system in the mixing reactor.

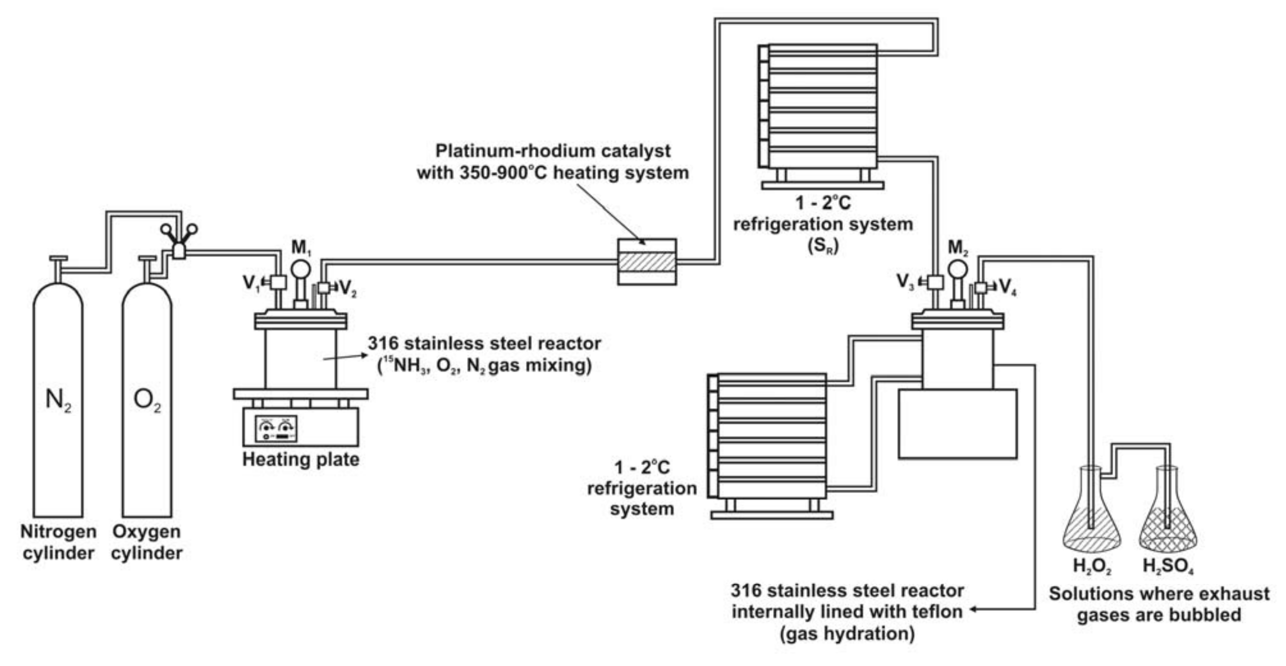

Figure 1: Complete system for the production of ^{15}N-enriched $H^{15}NO_3$ (double reactor)

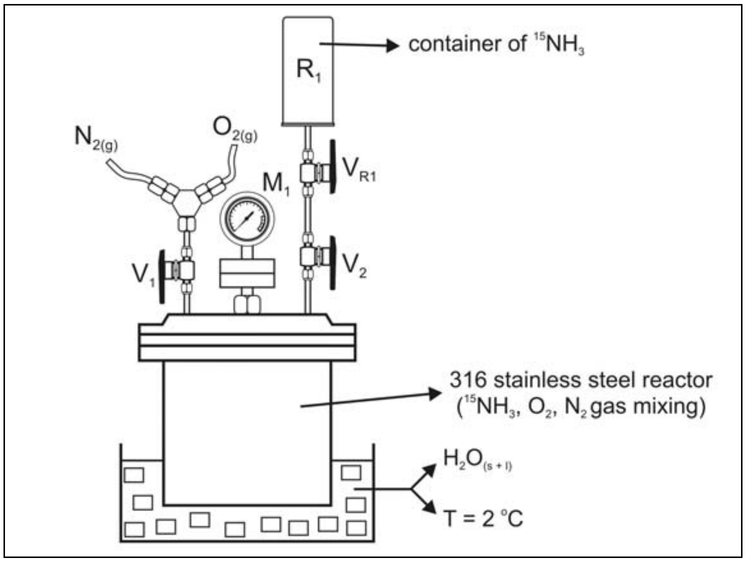

Figure 2: Gas loading system ($^{15}NH_3$, O_2, N_2) into the reactor

Figure 2 shows the stainless steel reactor (3 L) containing two inlets (V_1 and V_2). The O_2 and N_2 were admitted via V_1, while the V_2 valve admitted the previously-enriched anhydrous $^{15}NH_3$. Initially, prior to transferring the reagent gases into the reactor, its internal pressure was reduced by refrigeration (2°C) to facilitate gas admission. Then the R_1 container containing anhydrous $^{15}NH_3$ was connected to the V_2 valve and V_{R1} and V_2 were opened, transferring the gas into the reactor. The container was weighed and the mass (g) of $^{15}NH_3$ determined.

Using this value and the stoichiometric ratio (eq. 1), we determined the amount (mols) of O_2 to be transferred into the mixing reactor. This amount was admitted by V_1 and controlled by the reactor's pressure gauge, using the ideal gas equation. When needed, the inert gas N_2 was added (V_1) into the same reactor in order to maintain pressure in the system at the desired conditions.

$$^{15}NH_{3(g)} + 2\,O_{2(g)} \xrightarrow{H_2O_{(l)}} H^{15}NO_{3(aq)} \qquad (1)$$

Next, the mixture of gases ($^{15}NH_3$, O_2, and N_2) in the mixing reactor was heated to 110 ºC on a hot plate (Figure 1) for 10 minutes. At the same time, the catalyst was heated in an infrared oven equipped with a temperature controller. After heating both parts of the system, V_2 was opened and the gases were conducted through a stainless steel pipe (diameter ¼ inch) until reaching contact with a fine screen (8g), disposed in several layers, consisting of platinum (90 %) and rhodium (10 %). In this step, the anhydrous $^{15}NH_3$ was catalytically oxidized and converted into ^{15}NO, according to Ostwald's industrial method (Tageder and Mayer, 1980). The velocity of the catalytic reaction is very rapid, giving conversion in a short contact time (3.10^{-4}s) (Swaddle, 1997).

Next, the ^{15}NO containing excess O_2, needed for the oxidation process, was cooled by a cooling coil (S_R) (Figure 1), using H_2O as cooling fluid. As the resulting gases cool down, the ^{15}NO formed reacts with the O_2 present in excess, forming $^{15}NO_2$. This reaction is a slower oxidative process, but equilibrium is favored by a reduction in temperature (Shreve and Brink, 1977). In this process, the formation of $^{15}N_2O_4$ may occur.

Finally, the V_3 valve was opened, displacing the gases into the stainless steel reactor (2 L) at a constant flow, where most of the ^{15}NO not yet oxidized to $^{15}NO_2$ was then converted by the excess O_2. Next, when the pressures at the M_1 and M_2 manometers became equal, two procedures were employed to evaluate the effectiveness of the production process. In the first procedure, which used a complete flow of gases, valve V_4 was opened and the gases were exhausted (30 minutes), passing through a recovery system. Finally, valves V_4, V_3, and V_2 were closed, in this order. In the second procedure, which used partial flow of gases, valves V_3 and V_2 were closed, in this order, and valve V_4 was opened, causing only the hydration reactor gases to be exhausted, passing through a recovery system. Finally, valve V_4 was closed, and the gases that were in the mixing reactor, containing mainly anhydrous $^{15}NH_3$, were recovered to be reused in the process.

In the reactor, $^{15}NO_2$ was absorbed in H_2O, forming $H^{15}NO_3$ at a variable concentration, depending on the evaluated parameters. The process used here is different from the industrial method (Tageder and Mayer, 1980) with respect to the replacement of the absorption tower with a stainless steel reactor (internally lined with polytetrafluoroethylene) containing refrigerated H_2O (2 °C), in order to hydrate the $^{15}NO_2$. This absorption reaction is favored because of the reduced volume in the production system and the use of high pressure values (0.80 to 1.2 MPa), according to Le Chatelier's principle (Shreve and Brink, 1977). In the reactor, the reactions of $^{15}NO_2$ absorption in H_2O and ^{15}NO oxidation with residual O_2 were processed simultaneously (Cekinski, 1990).

After absorption, the exhaust gases, possibly containing gases such as N_2, residual O_2, ^{15}NO, and $^{15}NO_2$, underwent an oxidation process using H_2O_2, at the exit of the hydration reactor. These exhaust gases may also contain possible traces of $^{15}NH_3$ not converted in the process, which is neutralized in a 2.5 mol L^{-1} H_2SO_4 solution.

At the end of the process, the hydration reactor was opened and the solution ($H^{15}NO_3$) contained inside it was transferred to a proper reservoir (amber flask); the N content (N-NH_4^+ and N-NO_3^-) was then determined by distillation and titration (Trivelin et al., 1973). This procedure was also used to analyze the solutions obtained from the recovery system, in order to obtain the overall nitrogen balance (in relation to initial $^{15}NH_3$). The isotopic determination (% in atoms of ^{15}N) to verify the isotopic abundance of the final product was performed in an ATLAS MAT model CH4 mass spectrometer (Mulvaney, 1993).

Experimental Design

The process output for $H^{15}NO_3$ production was verified based on the following parameters: reaction temperature (350 to 900 ºC); ratio between reagents (Stoichiometric, 25, 50, and 100 % excess O_2) and flow of gases (total or partial).

The best conditions regarding reaction temperature, ratio between reagents, and flow of gases were used to evaluate process output in relation to the following parameters: flow of NH_3 through the catalyst (0.02; 0.04; 0.20; 0.62; and 3.39 g.min^{-1}) and system pressure (0.2; 0.34; 0.49; 0.64; and 0.78 MPa).

The tests were conducted with three replicates, according to a completely randomized experimental design, in factorial combination. The means were submitted to statistical analysis (Tukey 5 %).

Finally, tests were run with three replicates, aimed at the production of $H^{15}NO_3$ enriched at 90 % in atoms of ^{15}N, at the best conditions for the (physicochemical) parameters evaluated.

RESULTS AND DISCUSSION

The statistical analysis of data on temperature and reagent amounts showed an effect of these factors and their interactions on the $H^{15}NO_3$ production process. Table 1 presents data on mean conversion output (N-NH_3 to N-NO_3^-) and overall nitrogen balance (in relation to initial NH_3), as a function of reaction temperature and excess amount of O_2, using total flow of gases in the mixing reactor. The best results were obtained at temperatures of 500, 600, and 900 ºC for 50 and 100 % excess O_2. Although no statistical differences were observed among the results, the increase in reaction temperature was disadvantageous, due to the fact that during the tests a reduction in catalytic activity was verified: the catalyst had a usable life of 150 batches (tests). This phenomenon, defined as deactivation, is a strong chemisorption of reagents and impurities on the active sites of the catalyst, causing changes on the metal surface. Therefore, the best conditions for the production system were obtained when a temperature of 500 ºC was used for 50 and 100 % excess O_2.

Table 1: Conversion output (N-NH_3 to N-NO_3^-) and overall N balance (in relation to initial N-NH_3) as a function of parameters 'reaction temperature' and 'excess amount of O_2', using total flow of gases.

T (ºC)	Conversion (%)				Overall N balance (%)			
	Excess amount of O_2 (%)				Excess amount of O_2 (%)			
	0	25	50	100	0	25	50	100
400	20.4 aB	25.6 aBC	21.7 aBC	21.7 aC	45.8 aA	49.7 aA	43.7 aAB	41.7 aAB
500	17.0 cB	32.7 bAB	41.7 abA	47.5 aA	33.6 bA	40.7 abAB	48.6 aA	51.2 aA
600	35.8 abA	31.5 bAB	41.9 aA	45.4 aAB	38.7 aA	35.2 aBC	43.6 aAB	47.7 aA
700	19.0 aB	23.0 aBC	19.8 aC	15.9 aC	32.2 aA	25.9 aC	34.2 aBC	28.4 aB
800	20.2 aB	17.4 aC	16.9 aC	18.9 aC	35.4 aA	31.5 aBC	29.3 aC	30.0 aB
900	27.5 bAB	41.2 aA	32.5 abAB	33.8 abB	33.5 aA	41.3 aAB	33.5 aBC	45.1 aA

Measurements followed by different lower case letters in the rows and upper case letters in the columns are statistically different by Tukey test at the 5 % probability level

It was also verified that the mean overall nitrogen balance results (Table 1) at 500 ºC and O_2 excess values between 50 and 100 % showed a 2 % difference, which is equivalent to R$20.00 per batch, when enriched $^{15}NH_3$ is used (90 % in atoms of ^{15}N), while the addition of 50 % excess O_2 has an additional cost of R$0.16. Therefore, the best conditions were obtained when 100 % excess O_2 was used at 500 ºC. Under these conditions, the conversion of 47.5 % was possible, and an overall nitrogen balance of 51.2 % was achieved. The difference to complete the nitrogen mass balance refers to actual losses, which might be related to the ineffectiveness of the $^{15}NO_2$ hydration step and the influence of residence time of the gases with the catalyst's active metal (Pt), causing undesirable reactions in the process (N_2 and N_2O formation).

The temperature variation (400 to 900 ºC) results indicated a low conversion output for temperatures of 400, 700, and 800 ºC, using total flow of gases in the mixing reactor. The low conversion obtained at 400 ºC can be attributed mainly to the ineffectiveness of the 1st oxidation (NH_3 to NO), as demonstrated by the overall nitrogen balance values (Table 1).

In order to maintain high pressure in the system, a partial flow of gases was used in the mixing reactor. The mean conversion and overall nitrogen balance results as a function of the amount of O_2 (0, 25, 50, and 100 % excess O_2) and reaction temperature (350, 500, 650, and 800 ºC), with three replicates, are presented in Table 2.

It can be seen that the best results (conversion and overall nitrogen balance) were obtained at temperatures of 500 and 650 ºC for 0 and 50 % excess O_2, without statistical differences. However, with regard to the means (Table 2), the best system operation condition was observed with the use of 50 % excess O_2 at 500 ºC, since the use of high temperatures in the catalysis oven may increase the catalyst's deactivation rate (usable lifetime). Another important fact that justifies the best conditions herein defined was the 5 % difference in the mean overall nitrogen balance results (Table 2) for excess O_2 values between 0 and 50 %. This difference is equivalent to R$51.00 per batch, using enriched $^{15}NH_3$ (90 % in atoms of ^{15}N), while the addition of 50 % excess O_2 in the production reaction costs R$0.16. At the best conditions, a conversion of 55.2 % was possible, and an overall nitrogen balance of 82.9 % was achieved. The difference to complete the mass balance refers to actual losses in the system, which were lower (about three times) than those obtained under total flow of gases. The reasons for these losses were an ineffective 2nd oxidation (NO to NO_2) and the occurrence of undesirable reactions (production of N_2 and N_2O), considering that no NH_3 was quantified in the gases exhausted from the hydration reactor.

By comparing the results in Tables 1 and 2, decreases in conversion output and overall nitrogen balance can be observed when low temperatures (350 to 400 ºC) as well as high temperatures (700 and 800 ºC) were used, in both gas flow conditions at the mixing reactor. However, at intermediate temperatures (500, 600, and 650 ºC), superior results were observed, especially at 500 ºC, where the highest process output was obtained. This result was obtained using partial flow of gases in the mixing reactor, with the addition of 50 % excess O_2 in the reaction (eq. 1).

Using the best conditions (temperature of 500 ºC, 50 % excess O_2 and partial flow of gases) established in the process and a mean mass of 1.8g NH_3 (0.366 % in atoms of ^{15}N), tests were carried out with three replicates to evaluate process output as a function of NH_3 flow through the catalyst and production system pressure. The gases were conducted with exhaust time of 30 minutes (hydration reactor).

Under these conditions, there was an influence on conversion output and on overall nitrogen balance as a function of NH_3 flow (0.02; 0.04; 0.20; 0.62; and 3.39 $g.min^{-1}$) through the catalyst. The results obtained (Table 3) demonstrated a significant difference ($P<0.05$) in conversion output for all times evaluated. However, it can also be observed that there were no statistical differences for overall nitrogen balance results at flow values of 0.62 and 3.39 $g.min^{-1}$, which were statistically different from other values. Consequently, the best conversion results were obtained using a NH_3 flow of 3.39 $g.min^{-1}$. Under this condition, a conversion of 62.2 % was possible, and an overall nitrogen balance of 86.8 % was achieved. Flow rates higher than 3.39 $g.min^{-1}$ were not studied due to operational limitations of the system (piping diameter).

An influence of pressure (0.20 to 0.78 MPa) on conversion output was also verified. The results obtained did not show significant differences ($P<0.05$) for pressure values from 0.20 to 0.64 MPa, for which mean conversion output was 55.2 ± 2.3 %, achieving an overall balance of 82.9 ± 1.7 %. However, there was a statistical difference at a pressure value of 0.78 Mpa; such reduction is mainly due to an operational difficulty of the system at high pressure values, near the reactor's safety valve limit of 0.98 MPa.

Table 2: Conversion output (N-NH_3 to N-NO_3^-) and overall N balance (in relation to initial N-NH_3) as a function of parameters 'reaction temperature' and 'excess amount of O_2', using partial flow of gases.

T	**Conversion (%)**				**Overall N balance (%)**			
	Excess amount of O_2 (%)				**Excess amount of O_2 (%)**			
(ºC)	**0**	**25**	**50**	**100**	**0**	**25**	**50**	**100**
350	14.3 aC	14.5 aC	15.1 aC	11.4 aB	66.9 bC	67.4 abC	69.2 aB	73.6 aA
500	47.4 abA	43.0 bA	55.2 aA	42.1 bA	77.7 abAB	74.8 bAB	82.9 aA	76.9 abA
650	49.0 aA	47.9 aA	48.6 aA	45.2 aA	83.7 aA	81.3 aA	79.8 aA	79.2 aA
800	33.3 abB	29.2 bB	38.4 abB	41.3 aA	72.5 abBC	69.6 bBC	77.7 aA	78.3 aA

Measurements followed by different lower case letters in the rows and upper case letters in the columns are statistically different by Tukey test at the 5 % probability level

Table 3: Conversion output (N-NH_3 to N-NO_3^-) and overall N balance (in relation to initial N-NH_3) as a function of NH_3 flow through the catalyst (Pt/Rh).

NH_3 Flow ($g.min^{-1}$)	**Conversion (%)**	**Overall balance (%)**
3.39	62.2 a	86.8 a
0.62	55.2 b	82.9 a
0.20	41.3 c	77.2 b
0.04	28.7 d	71.8 c
0.02	21.2 e	71.0 c

Means followed by different letters are different by Tukey test at the 5 % probability level.

The entire production process (batch) involving all steps described, using 1.8g anhydrous $^{15}NH_3$, was performed in 60 min. Therefore, based on the best conversion result (62.2 %) and using previously enriched $^{15}NH_3$, the production line has a daily capacity to obtain 1,020 mL of 0.05 mol L^{-1} $H^{15}NO_3$ solution (approximately 3.2g) enriched at 90 % in atoms of ^{15}N. The amounts produced (g), corresponding to two batches, can be considered adequate, since most research studies involving the ^{15}N isotopic technique use compounds enriched at about 5 % in atoms of ^{15}N. As a result, starting from 3.2g $H^{15}NO_3$ enriched at 90 % in atoms of ^{15}N and using the isotopic dilution technique, we were able to produce 62g $H^{15}NO_3$ enriched at 5 % in atoms of ^{15}N. The isotopic enrichment of $H^{15}NO_3$ occurs because of the ^{15}N isotopic concentration in the reagent (anhydrous $^{15}NH_3$), since no isotopic fractionation was verified in the conversion from N-$^{15}NH_3$ into N-$^{15}NO_3$.

CONCLUSION

The best conditions for $H^{15}NO_3$ production were: catalysis oven temperature of 500 ºC; 50 % excess O_2; use of partial flow of gases in the mixing reactor; pressure of 0.4 Mpa and NH_3 flow through the catalyst of 3.39 $g.min^{-1}$. Under these conditions, a conversion of 62.2 % (N-NH_3 into N-NO_3^-) was possible and an overall nitrogen balance (N-NH_3 + N-NO_3^-) of 86.8 % was achieved and 510 mL of 0.05 mol L^{-1} $H^{15}NO_3$ solution (90 % in atoms of ^{15}N) per batch were obtained, starting from 1.8g anhydrous $^{15}NH_3$.

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