Solubility of Nitric Oxide from combustion gases in different absorption solutions

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Highlights

- The best absorption of NO was found in HNO_3 (1.08 mol/l) at 35ºC and 5 bar.
- Development of the first thermodynamic model for HNO_3-H_2O-NO with 15% fitting.
- The HNO_3 offers selectivity towards NO compared to N and O_2 which are also part of the flue gases from hydrogen combustion.

1. Introduction

The main drawback of hydrogen combustion is the high amount of nitric oxide (NO) generated during combustion, being three times bigger than in fossil fuels production due to the higher adiabatic flame temperature of hydrogen [1]. Nowadays, the most common method to control NO during combustion is to reduce the temperature in the turbine to avoid the NO formation also decreasing the thermodynamic efficiency of the turbine [2]. Currently absorption technology has been investigated due to its advantages of being inexpensive and efficient, nonetheless due to the low solubility of NO it is difficult to find a suitable absorbent that can overcome gas-liquid resistance to mass transfer [3]. By finding the right absorbent liquid, absorption can be implemented as an innovative approach that will allow increasing the turbine temperature, maximizing the thermodynamic efficiency and having a lower consumption of hydrogen per kWh of energy generated. Three absorbent liquids (amines, ethanol and nitric acid) were evaluated to find the most suitable for NO absorption, optimal properties regarding temperature, pressure and concentration were evaluated. The best absorption (1.08 $\frac{mol}{L}$) was obtained in nitric acid (HNO_3) at 30%, 35ºC and 5 bar. A NRTL model is proposed to represent the process absorption and the thermodynamic equilibrium, obtaining a 15% fitting, being the first model proposed for NO-HNO_3-H_2O system.

2. Methods

The equipment shown in Figure 1 was used to measure the solubility of NO. The process begins placing the absorbing liquid in the reactor to be degassed using liquid nitrogen and vacuum. Once degassed, the reactor is connected to a PID, and heating is initiated until the desired temperature is reached. The PID allows to monitor and control the temperature inside the reactor with a PT100 sensor and the temperature in the heating jacket with a thermocouple. An insulation system using rock wool is used to avoid high temperature changes. Once the temperature is constant, the reactor is pressurized with NO and the pressure drop is monitored until pressure stabilization occurs. Finally, the difference in pressures is used to determine the solubility using the real gas law. The experimental conditions were:

1) Amines: alkanolamines (AMP, MDEA and TEA) at 1,3,5 and 7 bar and 318.15 K, due to the wide application in scrubbing that they have with CO_2, only primary and tertiary amines were selected because they do not form nitrosamines which are toxic compounds [4].
2) Ethanol at 318.15 K and 1 bar.
3) Nitric acid (HNO3): The concentrations evaluated were 10, 20, 30 and 40% HNO3, 1 bar and 318.15 K. The best absorption rate was found at 30% HNO_3, therefore at this concentration the solubility was evaluated at 1,2,3,4,5 bar and 318.15, 328.15, 338.15, 348.15 K.

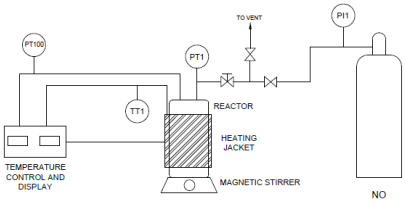

Figure 1. Experimental setup

3. Results and discussion

The best performance for amines was found for AMP (0.046 $\frac{mol}{L}$) at 7 bar and 35ºC, however the performance between the three types of amines was almost similar, having similar absorption rates as water (Figure 2). The low result for amines is because NO as a radical has faster reactions with other radicals to complete the electron pair, in the case of amines they have already the pair electrons, giving a low reaction rate. For Ethanol the best absorption rate (0.081 $\frac{mol}{L}$) was found at 7 bar and 35ºC being 2x higher than amines, due to the OH- has oxidant properties and can convert the NO into NO_2 (being the fastest reaction that NO can have), however it is limited by the availability of OH-. For HNO_3, the best result (1.08 $\frac{mol}{L}$) was obtained at 30%, 35ºC and 5 bar (Figure 3), this was achieved due to the ionization of HNO_3 when is in contact with water allowing to complete the HNO_3+ 2NO + H_2O -> $3HNO_2$. A thermodynamic model using NRTL and Peng Robinson equation was proposed for HNO_3-NO-H_2O system at 30% HNO_3, fitting of 15% was found between the experimental data and the results from the model.

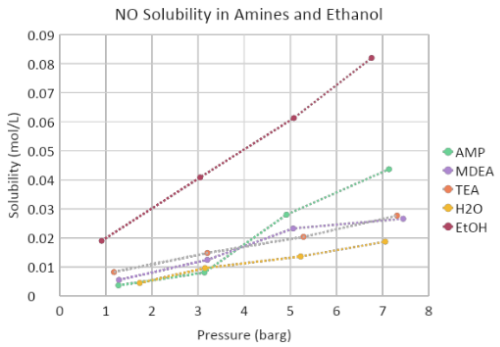

Figure 2. NO solubility in Amines and Ethanol.

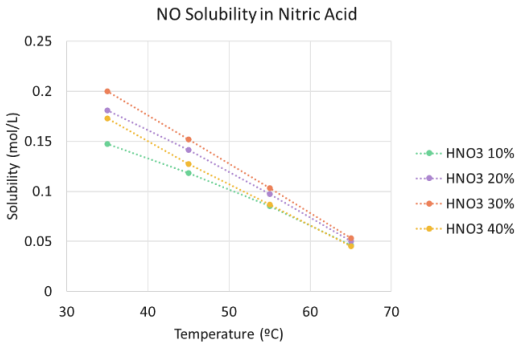

Figure 3. NO solubility in HNO_3

4. Conclusions

The highest solubility of NO was found in HNO_3 at 30% (1.08 $\frac{mol}{L}$) being 13x higher than EtOH (0.081 $\frac{mol}{L}$) and 23x higher than amines (0.046 $\frac{mol}{L}$). NO has low solubility in amines due to the low reactivity towards organic molecules. NO has medium solubility in alcohols due to the oxidation property of alcohols. NO has a very good solubility in HNO_3 due to the chemical dissociation of HNO_3 in water generating the NO_3^- radical. Using the best results for absorption a thermodynamic model using NRTL and Peng Robinson equation was proposed for HNO_3-NO-H_2O having a fitting of 15% between the experimental data and the model results.

References

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Keywords
Nitric oxide, Absorption, Nitric acid, Hydrogen combustion.