

Needle array DBD for solid urea decomposition

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Abstract—Selective Catalytic Reduction (SCR) of oxides of nitrogen (NO_x) by ammonia (NH₃) still is at the present the leading after-treatment technology for the NO_x removal process in diesel engines for stationary and mobile applications. A novel nonthermal plasma electrode in a needle array Dielectric Barrier Discharge (DBD) reactor powered by a high frequency neon transformer is used for the thermal decomposition of solid urea to produce ammonia. The urea thermolysis produces as byproduct besides ammonia the iso-cyanic acid which in turn can react with water in the gas phase (hydrolysis) giving ammonia and carbon dioxide. The presence of water fed before or after the plasma reactor is studied to increase the amount of produced ammonia

Index Terms— ammonia production, urea pyrolysis, DBD reactor, nonthermal plasma

I. INTRODUCTION

THE use of automobiles, trucks, power plants, industrial facilities and other sources, like residencies that burn fuel, are very common in these days. As a result, many undesirable products such as NO, NO₂, N₂O and CO₂ are produced from the combustion process. Among the unwanted products, nitrogen oxides (NO_x) play an important role in science and industry since the formation of nitrogen oxides is inevitable when fuel is burnt at high temperature in a combustion process. The formation of NO_x contributes to air pollution, causing acid rain and photochemical smog that destroy the environment.

The formation of nitrogen oxides occur through mainly three processes: Thermal NO_x, Fuel NO_x, and Prompt NO_x. “Thermal NO_x” is produced while nitrogen and air with excess oxygen are present at elevated temperatures (greater

than 1800 K) in the combustion processes. “Fuel NO_x” is formed in the combustion system reaction from chemically bound nitrogen in fuels such as coal, coke and heavy oils. “Prompt NO_x” is produced due to the breakdown of hydrocarbon fragments such as C, CH, CH₂ that may react with atmospheric nitrogen to produce other nitrogen species such as CN, H₂CN, HCN and NH under fuel-rich conditions. The oxidation of NO to NO₂ is part of the processes that result in the creation of ozone in the lower level of the atmosphere. Ground level ozone contributes to smog and causes human respiratory problems. On the other hand, ozone in the upper level of the atmosphere absorbs the ultraviolet rays from the sun creating the “ozone hole” [1-3].

Since the early 1970s, the importance of selective catalytic reduction (SCR) of nitrogen oxides (NO_x) has grown in the economical and technological aspects. SCR is the leading after-treatment technology for NO_x removal process in diesel engines for stationary and mobile applications. SCR is the process in which nitrogen oxides in the exhaust gas of diesel engine is reduced to nitrogen and water by reacting with ammonia in the presence of oxygen, as follows:



The general reducing agents for SCR process are ammonia (NH₃) gas or aqueous urea solution.

The Selective Catalytic Reduction (SCR) of oxides of nitrogen (NO_x) by ammonia (NH₃) over vanadium/titanium catalysts is an effective method for emission control from the exhaust of stationary diesel or natural gas engines. In an SCR system, an aqueous urea solution is injected into the exhaust where it evaporates and decomposes to ammonia and mixes with the exhaust before passing through a catalyst.

The simultaneous thermal and catalytic decomposition of urea has been examined for the selective catalytic reduction (SCR) of NO_x from mobile sources. The system was a fixed-bed flow reactor system, and a dual-reactor system in which the first reactor was for thermal decomposition and the second was for catalytic decomposition, specifically over copper exchanged ZSM5 catalyst. The role of the catalyst in the decomposition of urea into NH₃ and HNCO was negligible; urea decomposition occurs mainly by the thermal reaction. However, the catalyst was able to rapidly hydrolyze HNCO to NH₃ even at a temperature as low as 150°C. The catalyst also oxidizes NH₃ to N₂ in the presence of oxygen at reaction temperatures above 250°C.

Among many metal oxide supports, TiO₂ support has been found to be highly effective for the selective catalytic reduction of NO_x with NH₃ because of its durability to sulfur compounds. The sulfurization of the TiO₂ supported catalyst

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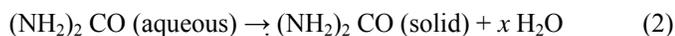
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has been found to even enhance the level of NO removal. Hence, due to its high activity and durability to sulfur compounds, V_2O_5 supported on TiO_2 is well known to be the most effective and widely used commercial catalyst for the SCR processes.

A ternary catalyst, $V_2O_5-WO_3/TiO_2$, was also recently introduced. Promoters such as WO_3 , SiO_2 and MoO_3 are usually added to V_2O_5/TiO_2 catalyst in order to enhance the catalyst activity. The promoters lead to the formation of acid sites on the surface of the catalyst, and the catalysts exhibit a higher catalytic activity than that of a single TiO_2 supported vanadium catalyst. The addition of WO_3 provides some poison resistance and improves NH_3 oxidation.

The thermal decomposition of urea and related compounds has been investigated based on TGA and DSC, together with the evolved gas analysis (EGA) with the help of an FTIR spectrometer. Compounds like biuret, ammelide and cyanuric acid as intermediate compounds were identified.

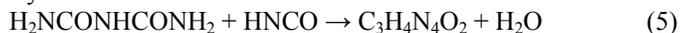
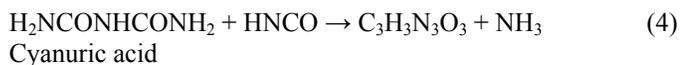
Studying the pyrolysis, despite the melting point of urea is $132.7^\circ C$, a complete melt of urea is not achieved until $135^\circ C$. Hence solid urea would melt after the urea injector to give molten urea. For urea water solutions the reaction starts with the complete evaporation of water molecules from the aqueous solution leading to solid urea:



Schaber et al. [19] mentioned that mass loss of urea began around $413 K$ ($140^\circ C$) and suggested 19 reactions for the urea thermal decomposition as the temperature rises. First, urea powder can be vaporized, and then NH_3 and $HNCO$ evolve around $425 K$ ($152^\circ C$). Biuret is produced from isocyanic acid reaction with urea through the following reaction:



Around $448 K$ ($175^\circ C$), cyanuric acid ($C_3H_3N_3O_3$) and ammelide ($C_3H_4N_4O_2$) are produced through the following reactions:



The products $HNCO$ and H_2O from reaction (5) and (6), react to form CO_2 at temperatures of about $700 K$ ($427^\circ C$). After $700 K$, NH_3 and CO_2 are produced as $HNCO$ is consumed from reaction (7).

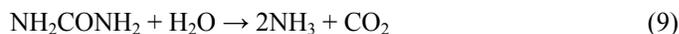


In studies about the thermal decomposition of urea, the mixture of urea and biuret was found at about $473 K$ ($200^\circ C$). The main component between $500 K$ and $600 K$ ($227^\circ C$ and $327^\circ C$) was cyanuric acid having a pale beige color deposit. Ammeline and ammelide having a dark beige color deposit were found as major components between $600 K$ and $700 K$ ($327^\circ C$ and $427^\circ C$).

NH_3 and $HNCO$ are the main decomposition products of dry urea. The main route up to $593 K$ ($320^\circ C$) seems to proceed through:



In presence of water, urea has been suggested to react:



The primary species from urea powder decomposition were $HNCO$, NH_3 , and CO_2 . Below $700 K$ ($427^\circ C$), $HNCO$ and NH_3 were dominant. The highest concentration of $HNCO$ was found around $650 K$ ($377^\circ C$), while NH_3 and CO_2 were detected increasingly after $700 K$ as $HNCO$ decreased.

The primary species from the decomposition of the urea-water solution were NH_3 and CO_2 . The amount of $HNCO$ was small compared to the decomposition of urea powder, but the highest amount of $HNCO$ was found at about $550 K$. The NH_3 and CO_2 concentration reached their maximum amount around $600 K$. After $600 K$, the amount of NH_3 and CO_2 decrease with a temperature rise. From these results, once water was injected, CO_2 started to be produced, while the amount of $HNCO$ decreased rapidly [4-22].

The main goal of the present research is to use a Dielectric Barrier Discharge reactor to convert solid urea powder into ammonia, studying the influence of the presence of water fed before and/or after the plasma reactor. Nitrogen is employed as carrier gas in dry conditions or bubbled into water for wet conditions. Feeding the nitrogen gas in wet conditions is studied with the purpose to increase the amount of produced ammonia, expecting to enhance the hydrolysis reaction of the intermediate compound $HNCO$ (isocyanic acid) to produce ammonia.

II. EXPERIMENTAL

The experimental setup is presented in Fig. 1 and consists of a DBD (Dielectric Barrier Discharge Reactor), a neon HV transformer, a digital power meter, an ammonia sensor and a Nitrogen gas cylinder. A thermometer (Hg) was placed into the reactor by the side of the exiting gases for the temperature measurements. The schematics of the reactor are given in Fig. 2. A flat horizontal electrode is covered by a 2 mm thick ceramic plate. Urea powder is placed on the ceramic plate with a stainless steel needle array (kenzan) electrode placed on top. The reactor is powered by a neon transformer (LECIP Co., Alpha M-5 $9kV_{o-p}$, $10kHz$, $28mA$ max) whose input power is monitored on the power meter (HIOKI HiTESTER). A 0-130V variable transformer is used to control input voltage to the neon transformer. The ammonia and other products concentration is monitored by an online FTIR (SESAM 3-N). This model of FTIR is intended to be used for the monitoring of the diesel gas and it requires a gas flow rate of minimum $4 L/min$.

For each experiment $160mg$ of urea powder is placed on the ceramic plate. For the nitrogen gas flow rates, $2L/min$ is fed at the entrance of the reactor, named "pre", $2L/min$ is fed at the

exit of the reactor, named “post”, and an additional 1L/min flow is fed downstream the reactor with the purpose of feeding in total 5L/min to the FTIR. The gas pippins to the reactor were both warmed up with a ribbon heater.

The working methodology is established as follows: Once urea powder is placed on the ceramic plate and the gas is flowed, voltage is applied (110V, 40W) during 1800 sec. The complete run is monitored by the FTIR.

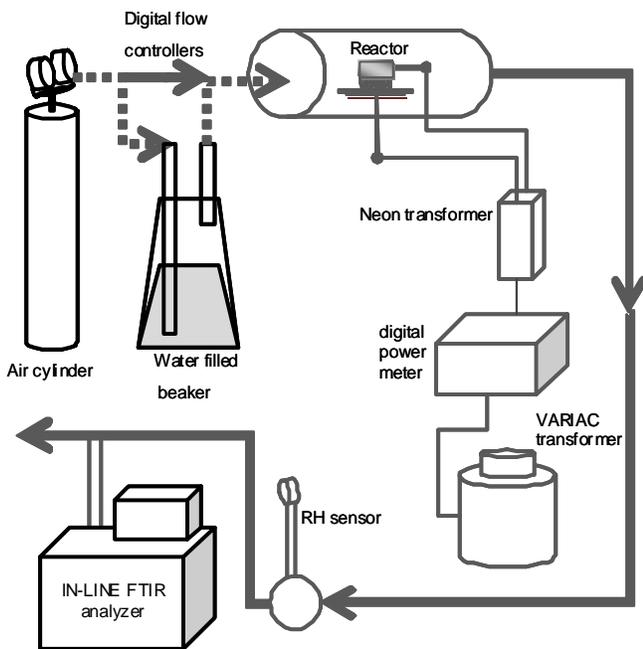


Fig. 1. Experimental setup.

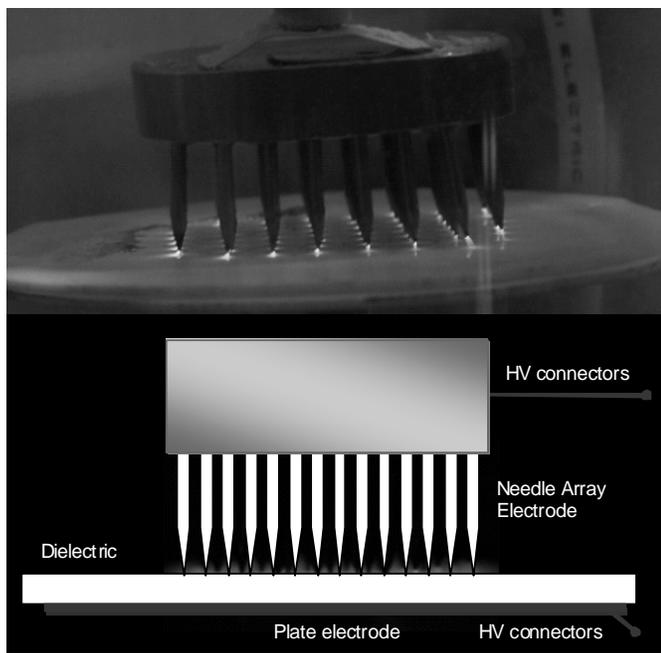


Fig. 2. Reactor.

III. RESULTS AND DISCUSSION

The experimental design techniques were used for planning the runs and posterior analysis of the results [24-26].

The input variable was water “yes” or “no” in the carrier nitrogen gas, that when is fed at the entrance of the reactor is called “pre”, and when fed at the exit of the reactor is called “post”. Table I display the water condition for the experimental runs.

TABLE I
WATER FEED CONDITIONS

WATER PRE	WATER POST
YES	YES
YES	NO
NO	YES
NO	NO

Fourteen runs of 30 min each one were carried out and the results obtained are shown in Fig. 3, Fig. 4, and Fig. 5, which display the ammonia (NH_3) concentration, the isocyanic acid (HNCO) concentration, and the cyanhydric acid (HCN) concentration vs time respectively.

Water concentration is not displayed but it was observed for all the experimental runs that during the first 15 minutes the concentration decreases around 20% and after that, no changes are produced up to the end of the runs. When the nitrogen carrier gas was bubbled into water at both, the “pre” and “post” positions, the initial water concentration was about 2%.

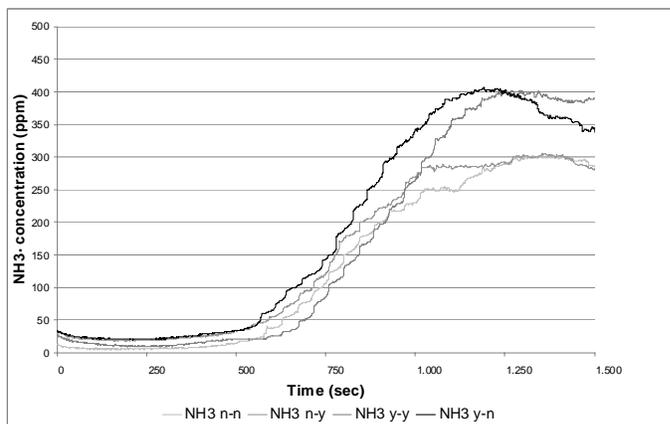


Fig. 3. Profile of NH_3 concentration (ppm), as a function of the experimental run time (sec). The symbols “n-n” stand for “no water pre”, “no water post” reactor, “y-y” stand for “yes water pre”, “yes water post” reactor, “n-y” stand for “no water pre”, “yes water post” reactor, and “y-n” stand for “yes water pre”, “no water post” reactor.

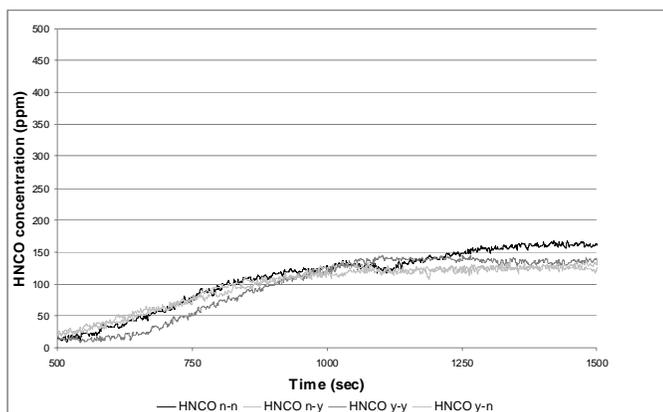


Fig. 4. Profile of HNCO concentration (ppm), as a function of the experimental run time (sec). The symbols “n-n” stand for “no water pre”, “no water post” reactor, “y-y” stand for “yes water pre”, “yes water post” reactor, “n-y” stand for “no water pre”, “yes water post” reactor, and “y-n” stand for “yes water pre”, “no water post” reactor.

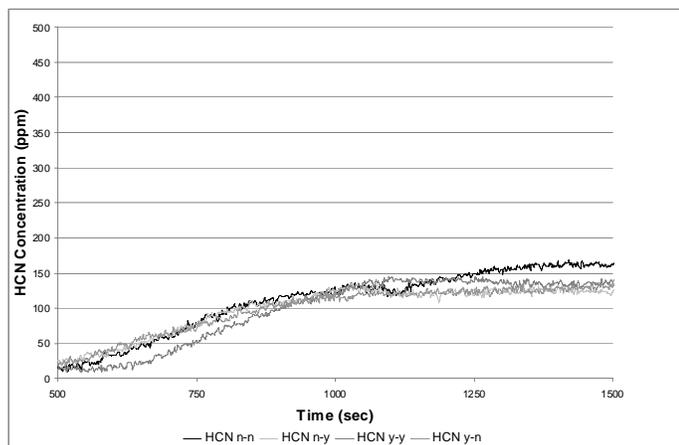


Fig. 5. Profile of HCN concentration (ppm), as a function of the experimental run time (sec). The symbols “n-n” stand for “no water pre”, “no water post” reactor, “y-y” stand for “yes water pre”, “yes water post” reactor, “n-y” stand for “no water pre”, “yes water post” reactor, and “y-n” stand for “yes water pre”, “no water post” reactor.

Ammonia (NH₃) production:

Figure 3 shows the profile of ammonia concentration along the 30 min of the experimental run, and clearly appears that “no water” or “water post” have the same effect on NH₃ production, reaching it a maximum concentration of 300 ppm. Nevertheless, the average yield is higher for “water post”.

For the case of “water pre”, which is the case of the carrier gas bubbled into water and supplied only at the inlet of the reactor, enhances the ammonia generation, reaching almost the same final value of 400 ppm as the case when water in the carrier gas is supplied at both, “pre” and “post” positions.

Nevertheless, the best conditions are reached when water is only supplied at the inlet of the reactor because along the whole

run the NH₃ concentration is higher.

Figure 3 also shows that similarly as with water, for all the runs carried out at the different conditions assayed, during the first 15 minutes the NH₃ production is rather low and with the same profile increases its concentration up to about 220 ppm from 0 sec to 900 sec.

Isocyanic acid (HNCO) production:

Figure 4 shows that the isocyanic acid concentration is almost no influenced by the presence or absence of water at the “pre” and “post” positions, and reaches a maximum value of 150 ppm. At difference with ammonia evolution, isocyanic acid starts growing from the beginning of the run, and similarly to the others compounds, after about 900 sec reaches a plateau, and an interesting observation is that when the carrier gas in wet conditions (“yes water pre”) at the beginning of the run HNCO shows the higher concentration and in turn the lowest concentration at the end of the run. This behavior could suggest that this intermediate compound is effectively converted to NH₃ due to a hydrolytic reaction, supported this observation also in the fact that for the “water pre” condition the highest concentrations of ammonia are obtained.

Cyanhydric acid (HCN) production:

Figure 5 shows that for dry conditions, which means “no water pre”, “no water post”, the HCN production reaches the maximum concentration with values about 14 ppm. The situation with “water post” enhances the no production of this toxic compound that grows slowly up to reach 6 ppm by the end of the run. The behavior with “water pre” and “water pre + post” is similar, reaching at most 4-6 ppm, being the best situation for not producing HCN the case with “water pre”, reaching only a concentration of 2 ppm.

When applying 110V with the neon transformer in the present DBD needle array nonthermal plasma reactor, the input power is about 40-50W, powerful enough for melting the urea powder. Urea starts melting after about 10 min of run producing a white smoke. According to the literature, under pyrolytic conditions 1 molecule of urea gives 1 molecule of NH₃ plus 1 molecule of isocyanic acid (HNCO), which in turn, undergo in a secondary reaction with 1 molecule of H₂O giving 1 molecule of NH₃ plus 1 molecule of CO₂ (reactions (7), (8), and (9)). The intention of feeding humid carrier gas upstream and downstream the reactor was to study the possibly enhancement of ammonia production through the intermediate compound (HNCO) reaction with water (hydrolysis). Results have demonstrated that the best situation is obtained when water is supplied upstream the reactor.

IV. CONCLUSION

A novel nonthermal plasma electrode in a needle array Dielectric Barrier Discharge (DBD) reactor powered by a high frequency neon transformer is used for the thermal decomposition of solid urea to produce ammonia. With an input power of about 40-50w, urea powder is melted undergoing in a thermolysis reaction that produces as byproduct besides ammonia the iso-cyanic acid which in turn can react with water

in the gas phase (hydrolysis) giving ammonia and carbon dioxide. The presence of water upstream or downstream the nonthermal plasma reactor is studied to increase the amount of produced ammonia. The best conditions for getting the highest ammonia concentrations are those obtained when the nitrogen carrier gas (2L/min) is humidified upstream the reactor, getting NH_3 concentrations of about 400 ppm. This novel electrode array resulted to be effective in producing NH_3 in a very simple operation that no needs the preparation of urea solutions and can be started at ambient temperature, showing hence much possibilities for a practical application.

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