

Analysis of the By-Products in the Ammonia Production From Urea by Dielectric Barrier Discharge

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Abstract—Ammonia, which is the main product of urea decomposition, is used as the reducing agent in the gas phase plasma NO_x treatment. Urea, because of its cheap price and relatively low decomposition temperature (150 °C), represents an excellent direct source of ammonia. In a dielectric barrier discharge (DBD), such temperatures can be achieved within a few minutes of applying voltage. This paper deals with the chemical analysis of the by-products formed by urea decomposition at about 150 °C–200 °C in a DBD, since it is well known that, depending on the temperature, urea decomposition by-products can be quite different. It was found that 0.25 g of urea used can be completely decomposed in several minutes at a constant input applied voltage of 9 kV (10 kHz). The main by-products are ammonia, isocyanic acid, and cyanuric acid. Moreover, it was found that dry and humid air showed no difference in the by-products formed.

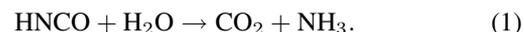
Index Terms—Ammonia, dielectric barrier discharge (DBD), FTIR, urea.

I. INTRODUCTION

UREA IS A white odorless solid with chemical formula $(\text{NH}_2)_2\text{CO}$. It is well known that urea decomposition gives ammonia as a main product and, depending on the conditions, isocyanic acid (HNCO) or CO_2 as by-products. Ammonia is used as the reducing agent in the gas phase plasma NO_x treatment [1]. It has been shown that the presence of ammonia in the gas feed greatly enhances the removal of nitrous and nitric oxides [2], [3]. Because urea decomposes thermally at about 150 °C, it represents an excellent direct source of ammonia. Although the available literature on urea decomposition by dielectric barrier discharge (DBD) is very scarce, some studies have been published [4]–[8]. In the work done in [4], the decomposition of solid urea by DBD was investigated, as well as the effect of gas humidity and type of catalyst pellets. In that study, apart from ammonia, no information of other by-products formed by urea decomposition was measured. This paper deals with the chemical analysis of the by-products, which are formed by urea decomposition at about 150 °C–200 °C in a DBD. It is well known that, depending on the temperature, urea decomposition by-products are quite different [9]. At about 152 °C, the

urea decomposition begins [10] forming ammonium cyanate ($\text{NH}_4^+\text{NCO}^-$). At 160 °C, strong NH_3 and HNCO peaks can be detected by a gas phase FTIR [11]. Between 160 °C and 190 °C, urea continues to vaporize and decompose, and HNCO can react with intact urea to produce biuret. Moreover, a cyanuric acid can be formed by the reaction of biuret with cyanic acid. As the temperature exceeds 190 °C, biuret starts to melt, giving cyanuric acid, ammelide, and ammeline. Reference [9] reported that the production of cyanuric acid, ammeline, and ammelide is completed at 250 °C, after which the sublimation and decomposition of products start to take place.

In this paper, the decomposition of 0.25 g urea by the DBD was investigated. It was found that the amount of urea used can be completely decomposed in several minutes at a discharge voltage of 9 kV. The main by-products are ammonia, isocyanic acid, and cyanuric acid. Isocyanic acid is a poisonous gas, but it can be easily removed by the following hydrolysis reaction:



Cyanuric acid is classified as “essentially nontoxic” [12].

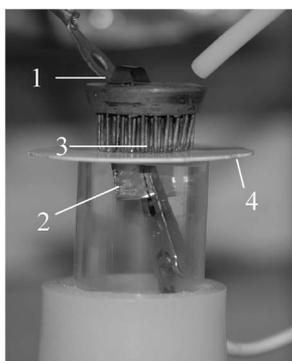
II. EXPERIMENTAL

Fig. 1 shows the experimental setup. The urea decomposition was performed in a closed glass vessel with the electrode configuration shown in Fig. 1(a). The experiment was performed as follows: 0.25 g of urea was placed and distributed on a ceramic plate (plate thickness: 2 mm; diameter: 6 cm). The upper metal electrode (electrode diameter: 3 cm) was circular in shape and consisted of evenly distributed needle-type points. This metal electrode was then placed on top of the solid urea. The lower flat horizontal metal electrode was attached at the bottom of the ceramic plate (this electrode cannot be seen from Fig. 1(a) due to the very low thickness of 1 mm). A neon transformer power supply (LECIP Company, Alpha M-5 9 kV_{0-p}, 10 kHz, and 28 mA max) was connected to the electrode at bottom of the ceramic plate and on the top of the needle electrode. Plasma formed in that manner was located around the tips of the metal needles just on the ceramic plate. The input voltage, adjusted by the 0–120 V variable transformer, and power were measured by a power meter (HIOKI HiTESTER), and all the experiments were performed at an input voltage of 100 V (9 kV). More detailed description is shown in Fig. 1(b). Air was introduced through the hollow metal tube at a flow rate of 10 L/min. In the

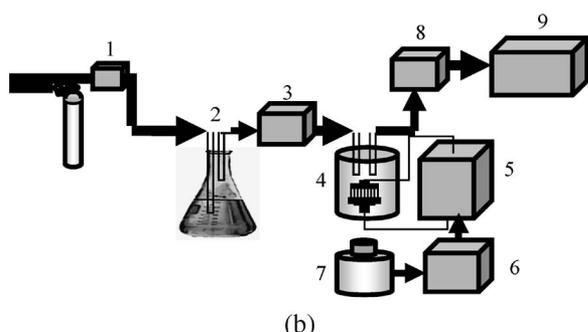
Manuscript received October 23, 2008; revised November 19, 2008. Current version published March 11, 2009.

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Digital Object Identifier 10.1109/TPS.2008.2011132



(a)



(b)

Fig. 1. Experimental setup. (a) Electrode configuration inside the reactor: (1), (2) HV connectors, (3) needle electrode, and (4) ceramic plate. (b) Experimental flow diagram: (1) Mass flow controller, (2) beaker with water, (3) relative humidity sensor, (4) glass reactor with electrodes inside, (5) neon transformer, (6) power meter, (7) variac, (8) NH_3 detector, and (9) FTIR.

experiment, where gas was humidified, the air stream passed through a beaker filled with water before entering the reactor. In that manner, humidity of around 69% was achieved. Ammonia concentration was measured by the $\text{NO}_x - \text{NH}_3$ detector. The detector sensitivity for ammonia was between 75 and 2290 ppm. Gas by-products were analyzed by the FTIR. Reflective FTIR was used for the analysis of solid residue that was not soluble in water. Anion ion chromatography was used for the analysis of water-soluble residue. Ammonium ions in water were analyzed qualitatively with Nessler reagents.

III. RESULTS AND DISCUSSION

A. Experiments Without Urea

The purpose of experiments without urea was to see the extent of NO_x formation by passing through a plasma zone. Fig. 2 shows the concentration of NO_x formed in the DBD from air when no urea is present on the ceramic plate. The experiment was run for 10 min, and clearly after approximately 4 min, the NO_x concentration started to reach a plateau with the final value of 55 ppm. FTIR spectroscopy confirmed that NO_x is actually all NO_2 .

Fig. 3 shows the FTIR spectra of the gases formed from air at 10 L/min with the spectra of the NO_2 standard. It is very clear that DBD in air produces NO_2 as the only major by-product. The characteristic NO_2 frequencies are 1608, 2229, and 2897 cm^{-1} , and these are marked as squares in Fig. 3. Moreover, colorimetric gas phase tube measurements revealed

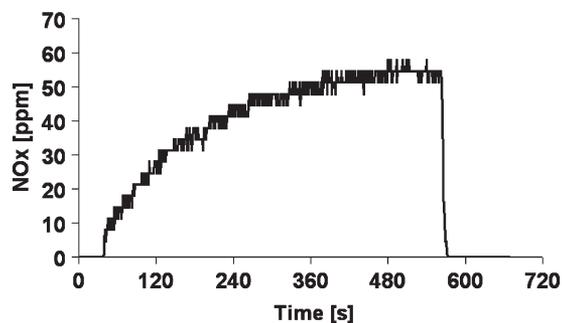


Fig. 2. NO_x formation from 10 L/min of air.

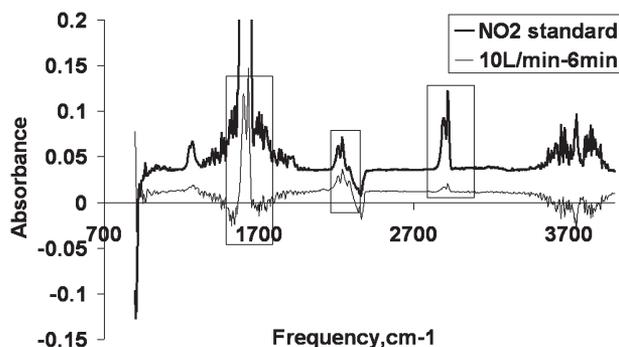


Fig. 3. Comparison of the FTIR spectra recorded after 6 min at 10 L/min with the original NO_2 standard.

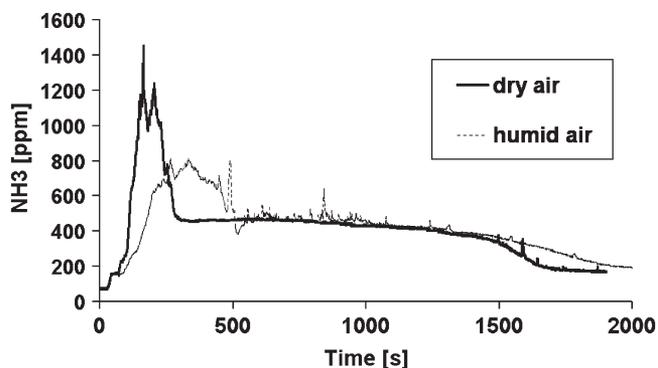


Fig. 4. Ammonia production from dry and humid air (a flow rate of 10 L/min and 0.25-g urea).

the presence of ozone (around 300 ppm), although the characteristic ozone frequencies were not found in the FTIR spectra. This was contributed to the slight delay between actual sample taking time and the measurement time in which ozone might have reacted.

B. Ammonia Formation From Urea in Dry and Humid Air

Fig. 4 shows the ammonia production from 0.25-g urea in dry and humid air. The calculated area under the curve (Simpson's rule) for both dry and humid air revealed that there is no significant difference between the two experiments. In numerical integration, Simpson's rule is a method for numerical integration, which is the numerical approximation of definite integrals. Specifically, function $f(x)$ is approximated by a series of arcs from quadratic functions and integrated across

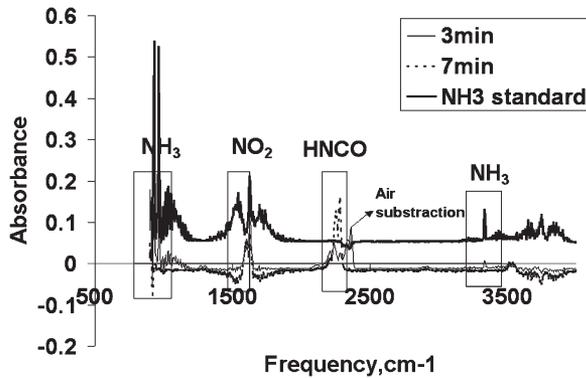
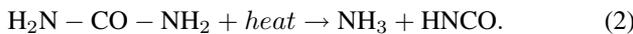


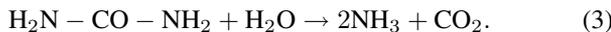
Fig. 5. FTIR spectra of the by-product formed by the urea decomposition in dry air after 3 and 7 min.

each of these. The concentration of ammonia formed by a decomposition of 0.25-g urea from dry air is 0.083 g, and from humid air, it is 0.086 g.

The urea decomposition takes place by the following equation [9]:



In the presence of water, a different mechanism could take place that would lead to a higher ammonia yield



The decomposition of 0.25-g urea, according to (2), should theoretically give 0.071-g ammonia. The calculated amount of 0.083 g from dry air represents approximately 17% error, which could be attributed to the calculated error when using Simpson rule to calculate the areas.

Fig. 5 shows the FTIR spectra of the by-products formed when dry air was used. The spectra compare samples taken after 3 and 7 min to the NH_3 standard. It is clear that NO_2 , NH_3 , and HNCO (cyanic acid) are the major by-products formed by the urea decomposition. After 7 min, there is a very slow rate of ammonia production that is also observed from Fig. 4. Fig. 6 shows the spectra of the by-products formed from urea decomposition at 13 and 23 min in dry air. It is clear that, after approximately 7 min, no new by-products are formed. NH_3 , HNCO , and NO_2 are the major by-products. Ammonia concentration is very low after 7 min.

Fig. 7 shows the FTIR spectra of the by-products formed when humid air was used. The spectra compare samples taken after 4 and 10 min. It is clear that NO_2 , NH_3 , and HNCO are the major by-products formed by the urea decomposition in the humid air. Fig. 8 shows the spectra of the by-products taken at 16 and 22 min. Again, as in the case of dry air, after approximately 10 min, no new by-products are formed. The major by-products are NH_3 , HNCO , and NO_2 .

It was observed that there was no difference in the by-products formed with or without water present. A proof that urea decomposition follows (2) lies in the absence of the CO_2 peak in the FTIR spectra. Carbon dioxide is formed by (3) when water is present, and quantitative analysis showed very similar amount of ammonia produced from both dry and humid air.

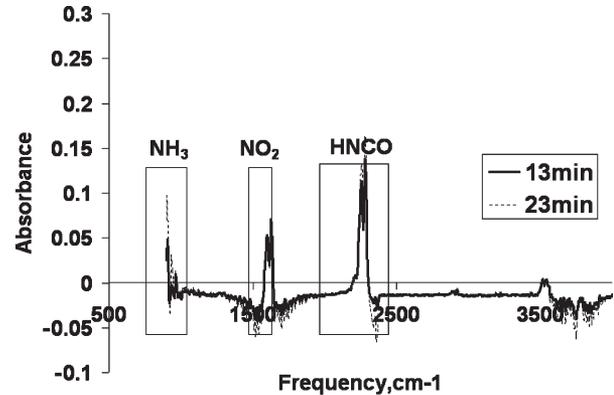


Fig. 6. FTIR spectra of the by-product formed by the urea decomposition in dry air after 13 and 23 min.

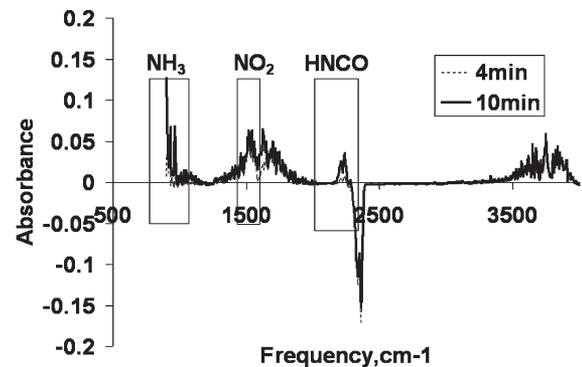


Fig. 7. FTIR spectra of the by-product formed by the urea decomposition in humid air after 4 and 10 min.

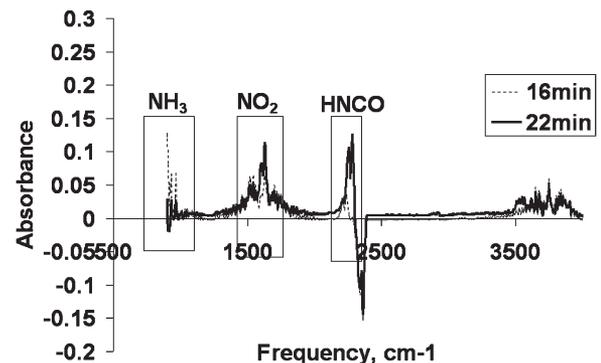


Fig. 8. FTIR spectra of the by-product formed by the urea decomposition in humid air after 16 and 22 min.

For ammonia to be produced by (3), the water molecule, as well as urea, has to be dissociated in the plasma zone to form radicals. It is highly possible that only urea was occupying the plasma zone, not allowing the water molecules to dissociate in the plasma.

Moreover, if the concentration of water was very low, the majority of water molecules would evaporate rather than break down in plasma.

It was mentioned in the introduction section that urea decomposition by-products strongly depend on the temperature; thus, the temperature measurements can be quite useful in understanding the urea decomposition chemistry and the by-products formation. In order to accomplish that, some further relatively

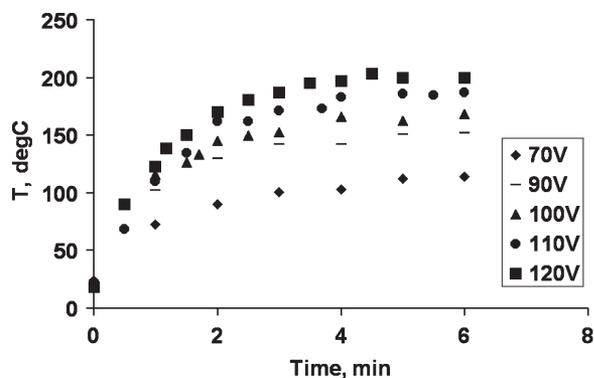


Fig. 9. Temperature measurement of the plate for different applied voltages.

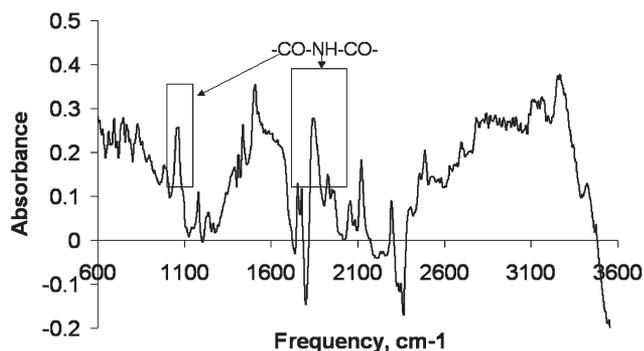


Fig. 10. Reflective FTIR spectra of the water-nonsoluble solid.

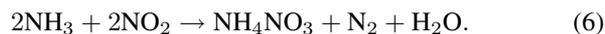
simplistic measurements were performed. Fig. 9 shows the temperature measurements in the plasma zone taken by the infrared temperature detector for the different input voltages. The same figure shows that, for 120 V, the maximum obtainable temperature is around 200 °C. Since all the experiments presented in this paper were done at 9 kV (100 V input voltage), the result in Fig. 9 indicates that the temperature around the plasma zone was approximately 150 °C. The temperature measurements shown in Fig. 9 are only valid for the vicinity of plasma and not for the inside of the plasma itself.

What was observed by the naked eye in the experiment was that, in the first few minutes of applying voltage, urea would melt into a solid mass. After that, there would be almost a sudden gas evolution from the melt. That is the time when the highest ammonia concentration is measured from both dry and humid air. During the experiment, a white powder was observed on the reactor walls and in the exit tubes from the reactor. This powder was soluble in water, and the colorimetric test for ammonia showed a positive result. It was concluded that the soluble white powder was ammonium cyanate ($\text{NH}_4^+\text{NCO}^-$). At the end of the experiment, the ceramic plate was covered in a different white powder which was soluble neither in cold (room temperature) nor in hot (heated) water at 70 °C. Fig. 10 shows the reflective FTIR spectra of the solid left after urea decomposition. The peaks at 1850 and 1059 cm^{-1} could be matched to cyanuric acid with characteristic bands representing cyclic imido configuration. The powder itself was soluble in hot water, which is also characteristic for cyanuric acid.

Based on the previously presented experimental evidence, it was concluded that urea decomposition proceeds according to the following mechanism. At approximately 150 °C, the urea decomposition starts according to



The FTIR spectrum in Fig. 5 confirms the presence of HNCO and NH_3 in the gas phase. Moreover, it is possible that solid ammonium cyanate ($\text{NH}_4^+\text{NCO}^-$), which is very light in structure (it has a flaky-type appearance), is blown away from under the electrode by the 10 L/min air passing through the reactor. Since there was also some white soluble powder found in the exit tubes from the reactor, ion chromatography was performed, and the presence of nitrate ions (NO_3^-) was confirmed. This could suggest that the following undesirable reaction is taking place:



In Figs. 6 and 8, it is shown that, even though the ammonium peak disappears, there is still HNCO peak present. If both HNCO and ammonia are formed from the same precursor ($\text{NH}_4^+\text{NCO}^-$), why is there a rise in the intensity of HNCO peak and not NH_3 peak? One can suspect that ammonia is involved in secondary (nonstoichiometric) reaction



At this point, the exact mechanism of the cyanuric acid formation is not clear. It was suggested by [12] that cyanuric acid could be formed directly from urea at 175 °C



IV. CONCLUSION

The decomposition of urea by the DBD in humid and dry air was studied. FTIR spectra showed no difference in the by-products formed in dry or humid air. The major gaseous products are NO_2 , NH_3 , and HNCO. NO_2 is formed from air in a maximum concentration of about 55 ppm, whereas ammonia and cyanic acid are formed via urea decomposition. Urea decomposition starts with the formation of ammonium cyanate, which then further decomposes to give ammonia and cyanic acid. The only solid product left after urea transformation is cyanuric acid. At a discharge voltage of 9 kV, approximately 5 min is needed for 0.25 g of urea to be consumed, where the maximum ammonia concentration is reached after only 2–3 min. At the reactor exit, there is a possibility of the undesirable reactions between ammonia and oxygen, and ammonia and NO_2 , but shortening the path from the reactor can prevent these. The temperature measurements of the reaction zone indicated that the temperature range of this system is high enough to melt urea and form ammonia but not too high to cause polymerization of the products.

Regarding the toxicity of the final by-products, HNCO is a toxic gas, but it readily hydrolyzes to give ammonia and carbon dioxide. Cyanuric acid is considered to be nontoxic.

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