Production of nitrogen containing organic species by non-thermal plasma over liquid butylamine

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Abstract: In this work, we investigate the formation of higher order nitrogen-containing organic compounds (NOCs) from butylamine in an effort to alleviate the high temperature and pressure requirements, and subsequently study the process's changing reaction chemistry with gas mixtures, reactor temperature, and treatment time. Under the optimized conditions, our proposed non-thermal plasma reactor was able to achieve a conversion efficiency of 49.4 g/kWh with pure argon gas at -20 ºC and formed compounds like aliphatic and aromatic amines, nitriles, and azoles.

Keywords: dielectric barrier discharge, nitrogen compounds, plasma chemistry

1. Introduction

Nitrogen-containing organic compounds (NOCs) are an essential class of chemicals used as agricultural chemicals, pharmaceuticals, water treatment chemicals, solvents, and rubber chemicals [1]. The production of such compounds follows an energy-intensive path producing substantial amounts of solid and liquid wastes, and greenhouse gases (GHGs). For instance, the synthesis of chiral amines requires multiple steps, in the form of N-substituted imines, enamines, and enamides, which lead to lower efficiencies [2,3]. In addition, industrial production processes require expensive nitrogen sources such as metallonitrene and azides that are both hazardous and toxic [4-6]. The common industrial practices of producing NOCs have thus been evolving with time to make the process more eco-friendly and sustainable.

The conventional practice of C-N bond formation was nitration followed by hydrogenation at high temperature and pressure with a Ni catalyst [7]. However, recently the most common method is to use amines with carbonyl compounds or direct C-N bond formation using Pd/Au catalysts [8,9]. The former is more popular as carbonyl compounds are easier to activate [10]. Schiff base reactions and reductive aminations, as they are known respectively, of the carbonyl compounds, pose problems like over-alkylation, alcohol formation, and catalyst reactivation [7]. Thus, using only a simple amine for direct C-H bond replacement, without any catalysts or carbonyl compounds, to form complex and valuable NOCs could be of great significance.

Emerging green technologies include photochemical and electrochemical methods, however, they have their own disadvantages. Photochemical methods require a stoichiometric amount of oxidant/reductant, whereas electrochemical methods have issues with undesirable over oxidation/reduction and/or electrode passivation [11]. These methods do not provide a novel solution for direct C-N synthesis, which directs our focus to explore alternate technologies for sustainable synthesis of NOCs.

In this regard, non-thermal plasma (NTP) can prove to be a notable solution, owing to its previous use in different fuel-reforming studies involving various carbon sources like alcohols [12-14], hydrocarbons [15-20], and a mixture of both [21]. NTP has the ability to produce highly energetic electrons at ambient temperature and pressure conditions. This non-equilibrium advantage of NTP allows thermodynamically unfavorable reactions to proceed at room temperature. In addition, using NTP for chemical reactions is also a flexible way of storing and using renewable electricity, which otherwise is difficult to handle due to its intermittent nature.

To our knowledge, very few NTP studies were conducted to synthesize NOCs. Recent studies that investigate direct NOC formation, especially liquid NOCs, were conducted by Yi. et. al. [22] and Hosseini et al. [23]. Yi et al. showed 0.46 and 0.82 g/L h of production of $(CH_3)_2NCN$ and NH_2CH_2CN, respectively, with 8.83% of CH4 conversion, while Hosseini et al. showed that direct synthesis of N-aryl compounds from toluene is possible with N_2 gas. These studies concentrate on synthesizing lower order NOCs, however, none of them investigates the conversion of lower order NOCs to higher order NOCs. They mostly use gaseous feeds which limit the use of various kinds of feedstocks. Furthermore, their low production efficiencies make industrial expansion unrealistic and their use of NH_3 is problematic due to difficulties with storage, handling, and high toxicity.

In this paper, we use a microsecond pulse dielectric barrier discharge (DBD) for the synthesis of NOCs. We use a DBD type gas discharge over liquid, which is known to have the ability to operate at room temperature with low energy requirement compared to in-liquid discharge, giving rise to higher production efficiencies. Butylamine was chosen as the simplest amine as lower order amines than are harder to handle in its liquid form due to the higher vapor pressures. Furthermore using a simple amine can alleviate the requirement of high pressure and temperature for synthesizing higher order amines, cutting down the energy costs. As reported in our group's earlier paper [21], we observed that a low temperature of -20 ºC increases the production efficiency of liquid products significantly as opposed to room temperature, and thus it was maintained across all studies except when we studied the effect of temperature. Different operating conditions are investigated to control or induce the reaction chemistry, knowing which, our proposed reactor could potentially be a sustainable alternative to the current NOC synthesis methods, for eg., the Schiff base reaction for amination.

2. Reactor Configuration

A two-gas-inlet microsecond pulse dielectric barrier discharge reactor was designed for our experiments, as shown in Fig 1. A pin-to-plate plasma configuration was developed using two stainless steel electrodes. The high voltage (HV) pin electrode was suspended in the gas phase and the grounded plate electrode was submerged in the liquid phase. The voltage in our experiments varied between ~ 20-25 kV and the current varied between ~ 200-400 mA, with a pulse frequency of 6 kHz. A constant discharge gap was maintained throughout all the experiments, with ~ 2 mm distance between the electrode and liquid surface such that the electrical characteristics are not influenced by the discharge gap. The electrical characteristics, like the voltage and the current, were measured using a Tektronix P650A voltage probe and a Pearson 411 current probe respectively. An electronic oscilloscope, Picoscope 2408B, was used to collect the measured data. The reaction vessel was jacketed and connected to a VWR recirculating chiller to control the reactor temperature. Argon and nitrogen gases were used for plasma discharge either individually or in a 1:1 mixture by volume. A total flowrate of 0.314 L/min was maintained across all the experiments, and the reactor headspace was purged with the feed gas for 10 min before beginning the plasma treatment. Our experiments were primarily conducted at -20 ºC, except for the temperature studies, with butylamine of 99.5% purity from Sigma-Aldrich.

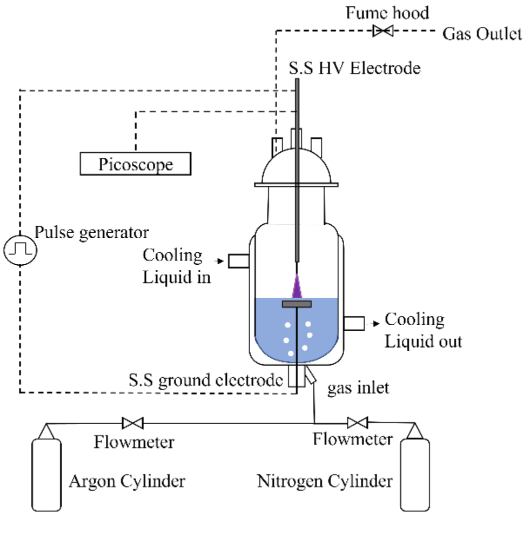

Fig. 1. Schematic of microsecond pulse pin-to-plate DBD reactor

3. Results and Discussion

A typical GC-MS trace has been obtained from the analysis of a butylamine sample after 1 h of DBD treatment generated in pure argon at -20 ºC. The corresponding compound names and structures have been determined by mass spectra and retention time and are shown in Fig 2.

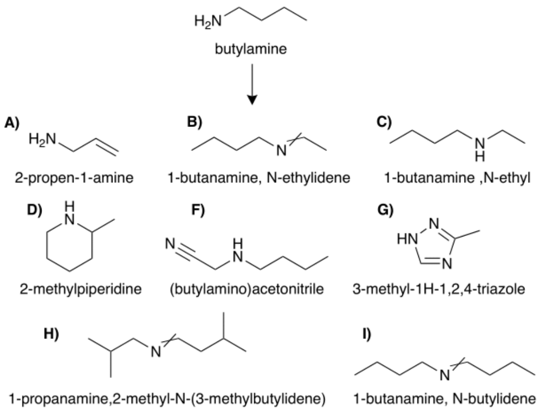

Fig. 2. Chemical structures of products obtained from plasma treatment

With the goal of maximizing the production efficiency of the nitrogen-containing compounds identified, we varied the gas supply between argon, nitrogen, and a 1:1 volumetric mixture of the two, while maintaining a constant total gas flowrate of 0.314 L/min. In our experiments varying the feed gas between argon and nitrogen does not yield any new products which indicates the absence of nitrogen fixation in our reactor system. Fig. 3. shows that plasma treatment with pure argon gas has the highest total production efficiency at 50.0 g/kWh, followed by the gas mixture and pure nitrogen at 10.7 g/kWh and 8.10 g/kWh respectively. This sharp decline in production efficiency with the introduction of nitrogen to the system can be justified by the presence of positively charged nitrogen ions in the high electric field formed between electrodes [24]. It is possible for these ions to consume free electrons in the field and react with other nitrogen ions to reform nitrogen gas, which inhibits the strength of the DBD on the liquid surface and reduces the overall production. This description agrees with the observation of the current in the system which decreases significantly with the introduction of nitrogen gas to the reactor.

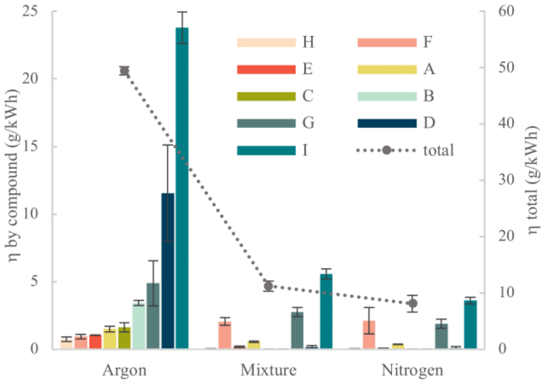

Fig. 3. Total production efficiency and production efficiency for each nitrogen-containing compound (g/kWh) with varying gas ratios after 1 hour at -20 ℃

Fig. 4. shows the production efficiency and selectivity of each nitrogen-containing compound with varying temperatures. The total efficiency decreases slightly with increasing temperature, from 49.4 g/kWh at -20 ºC to 44.2 g/kWh at 0 ºC and 43.9 g/kWh at 20 C, but this decrease is not the result of a reduced concentration of products. The total concentration of NOCs increases from 27900 ppm to 30600 ppm to 34000 ppm with increasing temperature, but the discharge power of the system also increases, from 21.0W to 25.9 W to 27.4 W which explains the decrease in efficiency. The temperature of the reactor is impacting the efficiency of the system due to substantial variations in gas dynamics with increasing temperature. The volatility of the butylamine liquid, whose vapor pressure increases tenfold, from 0.877 kPa at -20 ºC to 9.52 kPa at 20 ºC [25] indicates that an argon-dominated environment is only maintained in our reactor at lower temperatures. We also observed an increase in gaseous products in the form of a light grey gas forming inside the reactor after striking our plasma at 20 ºC. The increase in vapor-phase butylamine and the formation of new gas phase products explain the increasing breakdown voltages for plasma discharge with increasing temperature, and thus, the increased discharge power.

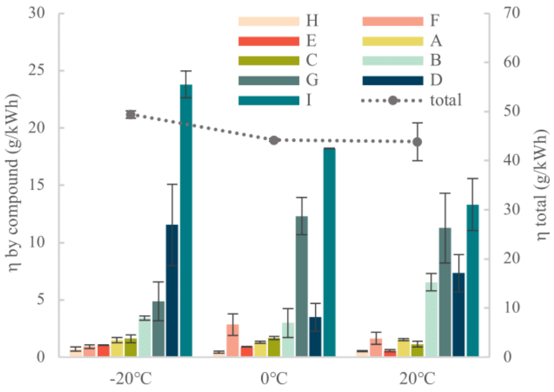

Fig. 4. Total production efficiency and production efficiency for each nitrogen-containing compound (g/kWh) with varying temperature after 1 hour with 100% argon gas

Fig. 5a. shows how the concentration of the synthesized compounds and the total concentration changes over a four-hour treatment period. The concentration values at each 15-minute interval do not lie outside the trend shown in the figure, so they are excluded for the sake of readability. The total concentration of NOCs increases from rom 2.66% to 5.91% to 9.24% to 13.6% hourly (mass %). When data from each 15-minute interval is included, the total concentration follows a linear trend of the form y=32247.6x with R2 0.997 where y is the concentration (ppm) and x is the treatment time (hours). Fig. 5b shows the production efficiency by compound and the total production efficiency (g/kWh) over time. The total production efficiency of the system is 60.7 g/kWh after 15 minutes and then hovers between 49.1 g/kWh and 51.8 g/kWh for the remainder of the 4-hour period. This slight decrease in efficiency is the result of the discharge power increasing after the first 15 minutes and then remaining constant which is attributed to carbon black buildup on the tip of the high voltage electrode which forms after a few minutes of discharge. There are three significant trends in production efficiency by compound with time. 1-butanamine, N-ethylidene (B) displays decreasing production efficiency with time, from 3.41 to 2.85 to 2.21 to 2.14 g/kWh. The compounds (butylamino)acetonitrile (F) and 3-methyl-1-H-1,2,4-triazole (G) display increasing efficiency with time from 0.934 to 1.15 to 1.46 to 2.33 g/kWh and 4.87 to 6.87 to 7.94 to 9.05 g/kWh respectively.

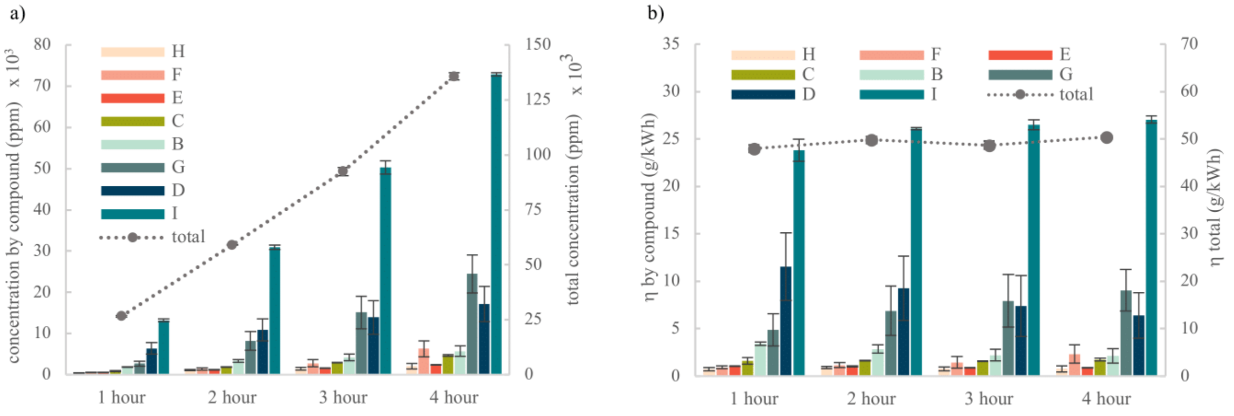

Fig. 5. (a) Total concentration and concentration by compound (ppm) variations with time at -20 C with 100\% argon gas and (b) Total production efficiency and production efficiency for each nitrogen-containing compound (g/kWh) with varying temperature after 1 hour with 100% argon gas

4. Conclusion

In this work, we demonstrate the synthesis of higher-order nitrogen-containing organic compounds using NTP, which can potentially alleviate the current stringent energy requirements of industrial production. Several products like amines, nitriles, and azoles were obtained through new C-N bond formation from butylamine. Further studies on parametric effects to understand the reaction chemistry showed that the gas mixture, reactor temperature, and treatment time have significant consequences on the production efficiency and the selectivity of the products formed. It is concluded that argon gas plasma is more effective for achieving higher production efficiencies (50.0 g/kWh) than nitrogen gas plasma (10.7 g/kWh) as its radicals have a tendency to recombine among themselves to N_2 gas instead of contributing to the reaction. Also, we observed higher production efficiency of 49.4 g/kWh at -20 ºC compared to higher temperatures of 0 ºC and 20 ºC with Ar as the carrier gas. Interestingly our production efficiency did not vary substantially with time although the concentration of the products increased linearly. The highest production efficiency was observed after 15 min of treatment after which there was a slight decrease to an almost constant value.

These results provide an interesting avenue for further investigations into such processes given the plethora of applications these compounds have in medicine, agriculture, etc. Further optimization and scale-up of the reactor could be possible by devising a continuous flow reactor as used in the falling water film experiments [26] with an appropriate catalyst, which could potentially help in overcoming the barriers of a batch system along with lowering treatment times for obtaining similar conversion.

5. References

[1] K. Hayes, Applied Catalysis A: General, 2001, 221, 187–195.

[2] D. Ghislieri and N. J. Turner, Topics in Catalysis, 2014, 57, 284–300.

[3] O. I. Afanasyev, E. Kuchuk, D. L. Usanov and D. Chusov, Chemical reviews, 2019, 119, 11857–11911.

[4] M. Sugiura and S. Kobayashi, Angewandte Chemie International Edition, 2005, 44, 5176–5186.

[5] A. R. Thornton and S. B. Blakey, Journal of the American Chemical Society, 2008, 130, 5020–5021.

[6] A. Dhakshinamoorthy and H. Garcia, Chemical Society Reviews, 2014, 43, 5750–5765.

[7] J. E. Kim, S. Choi, M. Balamurugan, J. H. Jang and K. T. Nam, Trends in Chemistry, 2020, 2, 1004–1019.

[8] J. Bariwal and E. Van der Eycken, Chemical Society Reviews, 2013, 42, 9283–9303.

[9] A. Trowbridge, S. M. Walton and M. J. Gaunt, Chemical reviews, 2020, 120, 2613–2692.

[10] A. F. Abdel-Magid, K. G. Carson, B. D. Harris, C. A. Maryanoff and R. D. Shah, The Journal of organic chemistry, 1996, 61, 3849–3862.

[11] Y. Yu, P. Guo, J.-S. Zhong, Y. Yuan and K.-Y. Ye, Organic Chemistry Frontiers, 2020, 7, 131–135.

[12] R. Shiraishi, S. Nomura, S. Mukasa, R. Nakano and R. Kamatoko, International Journal of Hydrogen Energy, 2018, 43, 4305–4310.

[13] T. Zhu, B. Sun, X. Zhu, L. Wang, Y. Xin and J. Liu, Journal of Analytical and Applied Pyrolysis, 2021, 156, 105111.

[14] B. Ulejczyk, Ł. Nogal, M. Młotek and K. Krawczyk, Energy, 2019, 174, 261–268.

[15] A. Hamdan, J.-L. Liu and M. S. Cha, Journal of Applied Physics, 2021, 129, 043303.

[16] G. SriBala, D. Michiels, C. Leys, K. M. Van Geem, G. B. Marin and A. Nikiforov, Journal of cleaner production, 2019, 209, 655–664.

[17] N. Khadir, K. Khodja and A. Belasri, Plasma Science and Technology, 2017, 19, 095502.

[18] Y. Ma, J. D. Harding and X. Tu, International Journal of Hydrogen Energy, 2019, 44, 26158–26168.

[19] Z. Wu, W. Zhou, X. Hao and X. Zhang, Energy, 2019, 189,116265.

[20] X. Zhang and M. S. Cha, Journal of Physics D: Applied Physics, 2016, 49, 175201.

[21] A. Banerjee, A. Golsztajn and P.-L. Girard-Lauriault, ACS Sustainable Chemistry & Engineering, 2022.

[22] Y. Yi, R. Zhang, L. Wang, J. Yan, J. Zhang and H. Guo, ACS omega, 2017, 2, 9199–9210.

[23] H. Hosseini, M. Saleem, E. Marotta and C. Paradisi, Plasma Processes and Polymers, 2021, 18, 2100012.

[24] M. Dhofir, R. N. Hasanah and C. Martineac, 2020 10th Electrical Power, Electronics, Communications, Controls and Informatics Seminar (EECCIS), 2020, pp. 76–80.

[25] C. L. Yaws, The Yaws handbook of vapor pressure: Antoine coefficients, Gulf Professional Publishing, 2015.

[26] V. V. Kovaˇcevi´c, B. P. Dojˇcinovi´c, M. Jovi´c, G. M. Rogli´c, B. M. Obradovi´c and M. M. Kuraica, Journal of Physics D: Applied Physics, 2017, 50, 155205.