

Plasma-catalytic synthesis of acrylonitrile from methane and nitrogen

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Abstract (AIChE J. max 150 words). In this work, we demonstrate plasma-catalytic synthesis of hydrogen and acrylonitrile (AN) from CH₄ and N₂. The process involves two steps: 1) plasma synthesis of C₂H₂ and HCN in a nominally 1:1 stoichiometric ratio with high yield up to 90% and high methane conversion > 90%; and 2) downstream thermocatalytic reaction of these intermediates to make AN. The effect of process parameters on product distributions and specific energy requirements are reported. If the catalytic conversion of C₂H₂ and HCN in the downstream thermocatalytic step to AN were perfect, which will require further improvements in the thermocatalytic reactor, then at the maximum output of our 1 kW radiofrequency 13.56 MHz transformer, a specific energy requirement of 73 kWh kg_{AN}⁻¹ was determined. The expectation is that scaling up the process to higher throughputs would result in decreases in specific energy requirement into the predicted economically viable range less than 10 kWh kg_{AN}⁻¹.

Keywords: Plasma-catalysis, electrification, methane pyrolysis, hydrogen production, nitrogen fixation.

Introduction.

Methane is an abundant natural resource. CH₄ typically comprises 75 to 90 mol.% of fossil natural gas.¹ It can also be produced anaerobically by decomposition of biomass to sustain the metabolic functions of organisms, wherein the product biogas is comprised of approximately 50 to 75 mol.% CH₄ with the majority of the balance gas being CO₂.² One of the principle technological uses of CH₄ is the production of hydrogen by steam reforming, which directly produces CO₂ in the water-gas shift step, and also indirectly produces CO₂ as a result of heat production for the endothermic syngas synthesis step. Thus hydrogen production by methane steam reforming is generally not considered sustainable unless it is combined with carbon dioxide capture and storage.³

Given electricity produced from renewable energy or nuclear energy, dehydrogenation of methane is much less energy intensive for producing hydrogen than water splitting. If the endothermic reaction is driven by electricity produced from wind power, for example, then the only CO₂ intrinsically emitted by methane dehydrogenation is produced from the primary source; for example, CO₂ impurities removed from raw natural gas. Quantitatively, producing hydrogen by complete dehydrogenation of methane is ideally six times less energy intensive than water splitting (Table 1). At the commercial scale, this gap remains, with water electrolysis requiring approximately 55 kWh kg⁻¹ of hydrogen;⁴ and recent reports on carbon black production at a scale of 10,000 tons per year⁵ from natural gas using thermal plasmas requiring as low as 12 kWh kg⁻¹ of hydrogen produced.⁶ The challenge is that the market for carbon black is approximately 10 million tons per year, which is about three orders of magnitude smaller than the amount of carbon that would be produced if the hydrogen economy were driven by dehydrogenation of methane. In general, the challenge with producing hydrogen by dehydrogenation of methane is identifying something useful to do with the carbon other than discarding it as waste.

Table 1. Reactions for producing H₂ without CO₂ emission. Specific energy requirement (SER)

	Stoichiometry	Ideal: ΔH_{298}^o	Industrial SER	Ref.
1.	$H_2O_{(gas)} \rightarrow H_2 + \frac{1}{2}O_2$	241.8 kJ mol ⁻¹	55 kWh kg _{H2} ⁻¹	⁴
2.	$\frac{1}{2}CH_4 \rightarrow H_2 + \frac{1}{2}C$	37.5 kJ mol ⁻¹	12 kWh kg _{H2} ⁻¹	⁶
3.	$\frac{2}{3}CH_4 + \frac{1}{9}N_2 \rightarrow H_2 + \frac{2}{9}C_2H_2 + \frac{2}{9}HCN$	130.5 kJ mol ⁻¹	TBD	This work

Structural materials, specifically concrete and steel, are currently produced at a scale of billions of tons per year. Since the structural material market may be large enough, we focus generally on structural materials produced from carbonaceous byproducts of methane dehydrogenation with the idea that these

materials may eventually replace concrete and steel in some applications. The vision is that these carbonaceous structural materials produced by methane dehydrogenation in the future are expected to resemble robust polymeric composites that are used today for advanced applications in aerospace, for example carbon fiber reinforced polyaryletherketones.⁷ These materials are also attractive for automotive applications, and the co-production of hydrogen could potentially lower production cost to make that application more economically viable.

The conventional process for synthesizing carbon fiber involves oxidizing and then graphitizing polyacrylonitrile fibers. Polyacrylonitrile is produced by polymerization of acrylonitrile. While it is a reaction that has only been discussed a few times to our knowledge in the public literature, highly exothermic synthesis of acrylonitrile can be accomplished by an addition of acetylene to hydrogen cyanide.⁸ The production of acetylene and hydrogen cyanide from methane and nitrogen results in less hydrogen than complete dehydrogenation to carbon black. However, it is still possible to produce hydrogen by this reaction using less electricity than water splitting (Table 1). Thus, there is a potential advantage from the perspective of electricity utilization for hydrogen production when compared to water splitting, and furthermore, the carbonaceous byproduct is more valuable than oxygen as a byproduct. The synthesis of acrylonitrile therefore seems attractive as a first demonstration of the production, by methane dehydrogenation, of a relevant carbonaceous material for structural applications. Furthermore, if the process is driven by renewable or nuclear electricity, then the reaction is expected to lower the CO₂ emissions required to produce acrylonitrile when compared to the industrial state-of-the-art Standard Oil of Ohio (SOHIO) process, which is relatively CO₂ intensive since it consumes hydrogen in the form of ammonia produced by the Haber-Bosch process.

In this work, we report a process concept for the plasma-catalytic synthesis of a carbonaceous material of relevance for structural applications, specifically acrylonitrile (AN, CH₂CHCN), by the dehydrogenation of methane. The process involves two steps. In the first step, acetylene (C₂H₂) and hydrogen cyanide (HCN) intermediates are synthesized by the reaction of methane (CH₄) and nitrogen gas (N₂) in a nonequilibrium plasma. Nonequilibrium plasma, in principle, can be less energy intensive when compared to thermal plasma as a medium for this reaction, due to the background gas temperature being lower. In the second step, the C₂H₂ and HCN intermediates react thermocatalytically to synthesize AN using a ZnO catalyst. The major impurity produced by this reaction is benzene when the gas fed to the thermocatalytic reactor is rich in acetylene, and the major impurity is propanenitrile when the gas fed to the thermocatalytic reactor is near the stoichiometric ratio of 1:1 C₂H₂:HCN. In both cases AN is a major product from the thermocatalytic reactor, thus proving the process concept. Focusing on the plasma reactor, adjusting 1) the reaction pressure, and 2) the hydrogen content of the nitrogen balance

gas, are found to be effective means to tune the $C_2H_2:HCN$ ratio of the intermediate product gas that elutes from the plasma. It is found that the specific energy requirement for the plasma, which is the power input divided by the ideal AN production rate, decreases with increasing feed rate at constant specific energy input. In other words, the reaction becomes more energy efficient as the throughput increases, which is a result that is very encouraging for scale-up. At the maximum output of our radiofrequency (RF) power supply, which is 1 kW, we measure an ideal AN specific energy requirement of $73 \text{ kWh kg}_{AN}^{-1}$. A preliminary technoeconomic assessment is presented that places this number in context of the SOHIO process and outlines future performance metrics at which the process presented herein is expected to be economically viable.

Methods.

The bench-scale experimental apparatus can be understood through the simplified process flow diagram presented in Figure 1. The reactor consists of two fluid systems. The plasma reactor fluid system operates at a reduced pressure in the range from 25 to 80 mbar; and the thermocatalytic reactor and gas analysis system operate near ambient pressure. A dry, chemical duty diaphragm pump (2090

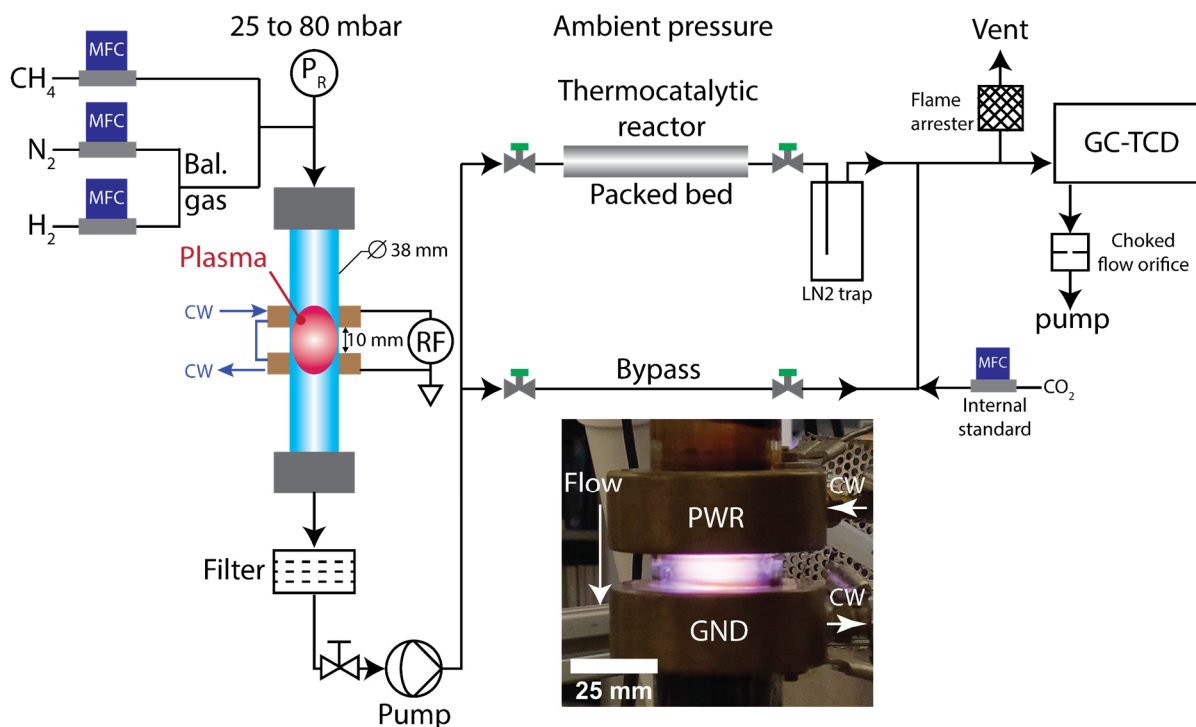


Figure 1. Schematic of the plasma-catalytic experimental apparatus. The inset is a digital image of the plasma during operation. Abbreviations: powered (PWR) and ground (GND) electrodes, flow direction and cooling water ports are labeled. Mass flow controller (MFC), balance (bal.), cooling water (CW), radiofrequency power supply 13.56 MHz (RF), liquid nitrogen (LN_2), and gas chromatograph with thermal conductivity detector (GC-TCD).

explosion proof, Welch, Mt. Prospect IL) was used to compress the flow from the pressure in the plasma reactor up to the pressure in the thermocatalytic reactor.

The plasma reactor consisted of a gas feeding system, reaction zone, and particle filter (Figure 1). The feed gases (CH_4 , N_2 , H_2) were controlled and measured by mass flow controllers (GE50A, MKS Instruments, Andover MA). For all experiments, unless otherwise stated, the mol fraction of CH_4 in the feed gas mixture was 19%. The balance gas, comprising the remaining 81 mol.% of the feed to the plasma, contained only N_2 and H_2 , with a variable composition depending on the experiment. The discharge tube was fused silica (Technical glass products, Painesville OH) and had an outer diameter of 38 mm and inner diameter of 32 mm. The plasma electrodes were brass rings that had a nominal inner diameter of 38 mm, an outer diameter of 63 mm, and a length of 23 mm. The gap between the powered and grounded electrode was 10 mm in all experiments. The electrodes were hollow and cooling water was used to prevent overheating, which becomes an issue in air-cooled configurations at applied powers greater than a few hundred Watts. The 13.56 MHz RF power supply (AG 1013, T&C Power Conversion, Rochester NY) had a maximum output of 1 kW. Specific energy inputs and specific energy requirements were calculated using the indicated forward power on the power supply. An automatic tuning network (AIT 600-R, T&C Power Conversion, Rochester NY) was used for impedance matching. Particle filters consisting of stainless-steel mesh affixed to KF centering rings were used to remove particulate byproducts formed during methane dehydrogenation. Particulate formation is unavoidable and must be dealt with even when that amount of carbon is only a few percent of the carbon fed to the plasma reactor. A throttle valve upstream of the diaphragm pump was used to control the pressure. The particle filters are necessary to ameliorate fouling and eventual clogging of the throttle valve, as well as fouling of the pump, which reduces pumping speed. Periodic cleaning of the pump and throttle valve is necessary. Furthermore, over long-term operation, up to an hour, carbon deposits between the RF electrodes will eventually cause a short circuit. To prevent short circuits, it is necessary to periodically etch the carbon deposit using H_2 plasma. Etches were typically done with 50% H_2 balance N_2 .

On the ambient pressure side of the diaphragm pump there were two flow paths. One went through the thermocatalytic reactor and a liquid nitrogen trap. The other flow path went through a bypass. These two flow paths downstream were sent to vent through a flame arrester. Before reaching the vent, a small portion of the flow, always less than the total flow, was sampled and sent through a gas chromatograph (8610C, SRI Instruments, Torrance CA) for compositional analysis. A ShinCarbon (ST 100/120, Restek, Bellefonte PA) column was used in combination with a thermal conductivity detector (TCD). The gas chromatograph (GC) sample flow was extracted through a choked flow orifice using a vacuum pump. Over time, small clogs in the GC sample port caused the pressure in the sample loop to

drop, which made all peak areas decrease but the relative peak areas stayed the same. Thus, quantification was performed by measuring peak areas relative to a known flow of an internal standard. The internal standard was CO₂, which produced a peak in the chromatogram that was well-separated from all the product peaks of interest. The intermediate product gas mixture that eluted from the plasma was characterized by passing the flow through the bypass before GC sampling (Figure 1). The final product mixture was characterized by passing the intermediate gas mixture through the catalyst bed (Figure 1). Conversion of C₂H₂ and HCN were characterized by measuring the composition of the gas eluting from the thermocatalytic reactor using the online GC with the vapor trap at ambient temperature. The condensable vapor mixture was characterized by cooling the trap to liquid nitrogen temperatures and then analyzing the carbonaceous liquid found in the trap after warming up to ambient temperature. The carbonaceous organic liquid condensed in the trap was characterized offline using gas-chromatography mass-spectroscopy.

The ZnO catalyst used in this work was based on a previous report that basic metal oxides are promising for the synthesis of AN from C₂H₂ and HCN.^{9,10} The catalyst was 10 wt.% ZnO supported on a high surface area silica gel prepared by wet impregnation. The silica gel support was 35-60 mesh davosil grade 636 (Millipore-Sigma, Saint Louis MO) with a manufacturer reported pore size of 60 Å and specific surface area of 480 m² g⁻¹ measured by nitrogen adsorption using the Brunauer-Emmet-Teller (BET) technique. An amount of 22.2 g of catalyst was prepared by the following procedure. To 50 mol of deionized water was added 8.116 g of zinc nitrate hexahydrate (Millipore-Sigma, Saint Louis MO). The salt was allowed to fully dissolve, and then 20 g of silica gel was added to the solution and mixed thoroughly. In the fume hood, 16 hours were allowed to pass such that the liquid water evaporated leaving the zinc nitrate salt deposited on the silica gel support. This material was then packed into a 200 mm length of 12.7 mm outer diameter stainless steel tubing packed with stainless steel mesh at both ends to retain the catalyst material in the center. The tubing had Swagelok fittings on both ends. Bellows-sealed high temperature valves were placed on both ends of the length of tubing and the entire tube with catalyst inside was tightly closed. The tubing was wrapped with heating tape and a thermocouple was used to monitor temperature during calcination. The material was calcined at 500 °C under flowing air for 5 hours to form the ZnO catalyst. A caustic NaOH scrubber was used to remove and neutralize acidic nitrogen oxide gases given off during calcination. After calcination, the valves were closed to prevent exposure of the catalyst to the ambient environment and the length of tubing, including valves and heating tape, were mounted to the plasma-catalysis system. Thereby the tube that was used to prepare the catalyst became the thermocatalytic reactor in the plasma-catalysis system. The fresh catalyst was not exposed to the ambient atmosphere.

Experiments focused on the production of liquid mixtures containing AN for offline gas-chromatography mass spectroscopy (GC-MS) characterization were carried out using 22.2 g of 10 wt.% ZnO catalyst. For all experiments, the temperature of the catalyst bed was 500 °C during reaction. Approximately 420 standard cubic centimeters per minute (SCCM) of total flow was passed through the bed resulting in approximately 20 SCCM per gram of catalyst. The effluent from the thermocatalytic reactor passed through the liquid nitrogen trap to collect condensable vapors. *Caution: HCN is an acutely toxic and volatile substance so its accumulation should be avoided. The liquid nitrogen trap, in which it is possible to accumulate uncreated HCN, should be opened in a properly functioning fume hood, and any product liquid transfers should also be carried out in a fume hood.*

The GC-MS protocol to analyze AN-containing reactor liquid samples utilized an Agilent 7890A GC equipped with a dual detection using an Agilent 5975C MS system with a triple-axis detector and a flame ionization detector (FID). A Polyarc® microreactor was installed upstream of the FID detector which enabled quantification via a single internal standard. Therefore, 100 µL of AN-containing sample was spiked with 1 µL decane standard. The Polyarc converts all carbon to methane so moles of a species in the sample is proportional to the GC peak area divided by the number of carbons in the compound. GC analysis was performed using a Restek fused silica RTX-50 capillary column (crossbond phenyl methyl polysiloxane, ID: 0.25 mm, film thickness: 0.5 µm, and length: 30 m). The inlet temperature was set at 250 °C with a split ratio of 100:1, and the helium was held at 26 mL/min. 0.2 µL of AN-containing sample was injected every run. The column temperature was held at 40 °C for 2 minutes and then heated to 315 °C and held at that temperature for 55 minutes. The MS detector was held at 285°C and no solvent delay was applied. The MS spectra were identified by using the system database (pal600k.l, Wiley, USA) while external standards were used to verify peak assignment of compounds of interest.

In select experiments, plasma diagnostics were carried out to further characterize the reaction environment. The voltage applied to the powered electrode was measured with respect to the grounded electrode by means of a 1000× high voltage probe (P6015A, Tektronix, Beaverton OR) connected to an oscilloscope (2014C, Tektronix, Beaverton OR). The background gas temperature was characterized by inserting a fluorescence decay temperature probe (OptoTemp 2000, Micromaterials Inc., Tampa FL) with an operational range from 200 to 950 °C into the plasma.¹¹ The temperature probe was positioned just downstream of the powered electrode in the discharge gap.

Results and Discussion.

The basic idea behind our approach to plasma-catalysis involves activating the gas in the plasma, followed by downstream catalytic relaxation towards equilibrium to synthesize the desired products. The concept is illustrated in Figure 2. Consider a feed gas composition that is 19 mol.% CH₄ and 81 mol.% N₂. At the feed conditions, this gas is nominally in the equilibrium state at ambient temperature and the reactor pressure. In the discharge, the gas gets activated into an excited state that is stable only in the nonequilibrium plasma.^{12,13} As soon as the gas leaves the plasma, the time evolution is governed by the equilibrium state at the local temperature and pressure, and the chemical composition that was previously stable in the plasma becomes unstable and relaxes to a metastable state through a process termed recombination. This metastable product of the recombination process can then be observed by gas analysis equipment such as gas chromatographs.

It has become apparent recently that nonequilibrium plasmas produce metastable chemical configurations that are shifted in the endothermic direction with respect to equilibrium at the pressure and background gas temperature in the nonequilibrium plasma.¹³ These intermediate chemically metastable products of the endothermic plasma reaction can have very high enthalpy of formation, for example C₂H₂ and HCN. As such, the intermediate products are thermodynamically unstable at low temperatures and can be made to react exothermically by downstream thermal catalysis. By controlling the catalytic reaction using well-known approaches of thermal catalysis, desired final products can be produced. This approach allows independent optimization of the plasma reaction and thermal catalytic reaction. The plasma can be optimized to produce the desired intermediates with minimized specific energy requirement, desired stoichiometry, and yield of carbon. The thermocatalytic reaction can then be separately optimized using the catalyst material, amount of catalyst, temperature, etc. to maximize overall reaction objectives such as yield of final product (e.g. AN). This approach to plasma-catalysis is more

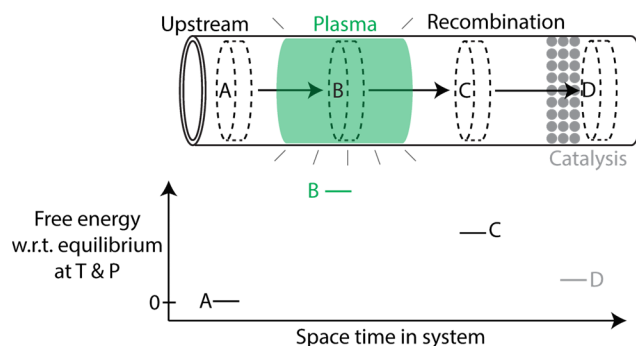


Figure 2. Plasma-catalysis concept. The feed gas is state A. The chemical state that is only stable in the plasma is B. The intermediate chemically metastable products observed from the plasma reaction is state C. The final product of the process after thermocatalytic relaxation is state D. Abbreviation: with respect to (w.r.t.).

robust than placing the catalyst in contact with the plasma because it is unlikely that energy-efficient, high-yield plasma conditions will overlap in parameter space with conditions that the catalyst can achieve high-yield of the desired final products.

In this work, the focus is primarily on the nonequilibrium plasma step with the goal of synthesizing $C_2H_2 + HCN$ intermediate products in equimolar ratio from methane and nitrogen feedstock. In other words, this work focuses on state C in Figure 2. However, we will also present a preliminary proof-of-concept for the overall process where the effluent from the plasma was directly passed through the thermocatalytic reactor and synthesis of final AN product was demonstrated. From these preliminary experiments, some first observations are made of the relationship of the C_2H_2 and HCN stoichiometric ratio to the impurities present in the synthesized AN.

Some definitions must be made to understand the performance of the process. 1) Specific energy input is defined as the power read from the power supply divided by the total influent molar flow rate to the plasma. 2) Throughput is the amount of mass and the amount of energy that is passed through the system per unit time while keeping the specific energy input constant. In other words, increasing throughput means increasing power and total molar flow rate proportionally while keeping everything else constant. 3) The yield of $C_2H_2 + HCN$ is the fraction of carbon that has been converted into $C_2H_2 + HCN$ with 1:1 molar ratio. Yield accounts for conversion of CH_4 , unwanted byproducts, as well as overproduction of intermediates (e.g. overproduction of C_2H_2 relative to HCN or vice versa). Quantitatively, the yield of the plasma reaction can be calculated from the measured molar flow rates of acetylene and hydrogen cyanide in the plasma effluent, and the molar flow rate of methane in the influent:

$$Yield = \frac{3 \cdot \min(\dot{n}_{C_2H_2}^{out}, \dot{n}_{HCN}^{out})}{\dot{n}_{CH_4}^{in}}, \quad (1)$$

Where $\dot{n}_i^{in/out}$ is the molar flow rate of species i into, or out of, the plasma. If the carbon in the methane is completely converted into $C_2H_2 + HCN$ in a 1:1 molar ratio, then the yield would be 100%. 4) The ideal AN production rate is defined as what the production rate of AN would be if the downstream thermocatalytic reaction has 100% yield of AN. 5) The ideal specific energy requirement of AN synthesis assumes a perfect downstream catalytic reaction and is thus determined by the limiting reagent in the $C_2H_2 + HCN$ mixture. Quantitatively:

$$SER_{AN}^{IDEAL} = \frac{\dot{W}_{in}}{M_W^{AN} \min(\dot{n}_{C_2H_2}^{out}, \dot{n}_{HCN}^{out})}, \quad (2)$$

where \dot{W}_{in} is the forward power read from the RF power supply and M_w^{AN} is the molecular weight of acrylonitrile, which is $0.053 \text{ kg mol}^{-1}$.

The yield from the plasma of acetylene and hydrogen cyanide increases with throughput at constant specific energy input. For an inflow composition of 19% CH_4 balance N_2 , the yield of $\text{C}_2\text{H}_2 + \text{HCN}$ is plotted as a function of total influent molar flow rate to the plasma for several different specific energy inputs in Figure 3a. The high flow limit in the plots was determined by the maximum output of the power supply (1 kW). The error bars were determined by repeat experiments at nominally the same conditions. The standard deviation of the measurements was approximately $\pm 10\%$ of the value. Since the yield of $\text{C}_2\text{H}_2 + \text{HCN}$ increases with throughput at constant specific energy input (Figure 3a), the ideal specific energy requirement of AN synthesis decreases with increasing throughput (Figure 3b).

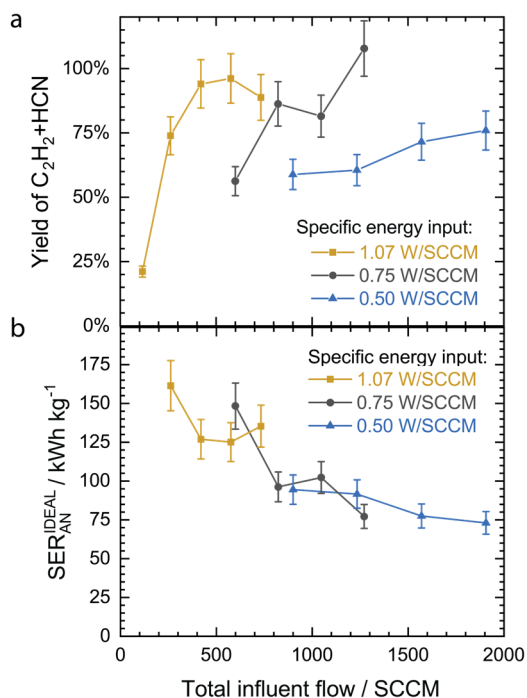


Figure 3. Increasing throughput at constant specific energy input increases yield and decreases specific energy requirement of AN synthesis. All experiments were conducted using 19 mol.% CH_4 balance N_2 influent at a pressure of 53 mbar. Yield was calculated using equation (1) and specific energy requirement using equation (2).

The results in Figure 3 demonstrate that the energy efficiency of the process can be tuned by changing the power supplied to the plasma and the total influent flow rate. Importantly, the data in Figure 3 shows that the reaction becomes *more energy efficient* when the throughput increases. This result is very encouraging for scale-up. Reactors with higher production rates are expected to have lower specific energy requirement for producing AN. Unfortunately, our current apparatus does not allow for increasing

the throughput beyond what is plotted in Figure 3. A system with a larger RF power supply and higher flow rate capacity would be required to test the hypothesis that the specific energy requirement continues to decrease at higher applied powers and higher total flow rates. Interestingly, the results in Figure 3 are already competitive with the few results that have been reported for thermal plasmas for this reaction.^{14,15} The comparison to thermal plasma is encouraging in that nonequilibrium plasmas, which have a lower background gas temperature compared to thermal plasmas and therefore require less bulk gas heating, may ultimately be more energy efficient.

It is instructive to break out in detail the results for our condition that produces the lowest specific energy requirement. That data will provide context for the development of parameters to tune the output from the plasma reaction. The detailed plasma operational conditions, as well as inputs and outputs for the most energy efficient case we have thus far measured are presented in Table 2. Examination of the data in Table 2 reveals that the methane conversion is very high, 95.6% of the carbon fed into the reactor as methane has been converted into other species. Nearly all of this carbon has been converted to acetylene and hydrogen cyanide, with less than 1% of other C₂ species such as ethylene and ethane. The challenge is that the acetylene and hydrogen cyanide are not in the stoichiometric ratio. More specifically, for an ideal 1:1 molar ratio of C₂H₂:HCN, there needs to be 2× more carbon in C₂H₂ compared to HCN. Inspection of the data in Table 2 reveals that the carbon in C₂H₂ is approximately 2.8× the carbon in HCN. In other words, there is too much acetylene in the product gas stream – the molar ratio C₂H₂:HCN is approximately 1.4:1. Complicating the situation, the C₂H₂:HCN ratio changes with throughput. For the data in Figure 3, the C₂H₂:HCN ratio varied from 1.8:1 (C₂H₂ rich) to 0.83:1 (HCN rich). In the future, as the process is tuned to minimize SER_{AN}^{IDEAL} by increasing the throughput, methods are needed to adjust the effluent composition at a given throughput to bring it back to the stoichiometric ratio. For example, if the carbon present in the C₂H₂ and HCN for the case in Table 2 were redistributed such that the C₂H₂:HCN ratio were stoichiometric, then the SER_{AN}^{IDEAL} would drop to 57 kWh kg_{AN}⁻¹. We therefore next discuss experimental parameters that allow the effluent composition to be tuned independently from throughput.

Table 2. Summary of plasma operational conditions, inputs and outputs for an example case with relatively low ideal specific energy requirement for AN. Note: raw data from additional experimental conditions is available in the online supplementary material.

Inputs		
Pressure	53	mbar
Background gas T	>1223	K

RF Power	953	W
Total input flow rate	1906	SCCM
CH ₄ input mol fraction	19	%
N ₂ input mol fraction	81	%
H ₂ input mol fraction	0	%
Outputs		
Yield C ₂ H ₂ + HCN	75.9	%
SER_{AN}^{IDEAL}	73.1	kWh kg _{AN} ⁻¹
Ideal AN production rate	13	g _{AN} hr ⁻¹
Fraction of carbon in effluent as:		
CH ₄ :	4.4	%
C ₂ H ₂ :	71.8	%
HCN:	25.3	%
C ₂ H ₄ :	0.16	%
C ₂ H ₆ :	0.13	%
Carbon balance:	-1.83	%

Reactor pressure and balance gas composition (N₂ and H₂) can be used to tune the composition of the plasma effluent. More specifically, HCN selectivity, expressed as the fraction of carbon in the effluent from the plasma, decreases with increasing H₂ fraction in the balance gas and with increasing reactor pressure. Plotted in Figure 4 are the results of experiments that were conducted at a constant total flow rate of 420 SCCM fed to the plasma, constant CH₄ mol fraction of 19% in the influent, and a constant RF power input of 450 W. Ethane and ethylene were also measured but were very low and have been omitted for clarity. The carbon balance is the carbon that was not accounted for as species measured by GC-TCD, which can be thought of as particulate and tar deposition in the reactor. Plotted in Figure 4a is the result of a triplicate of experiments conducted at a constant pressure of 53 mbar with different H₂ mol fractions in the feed. The remainder of the feed gas was N₂ that was not CH₄ or H₂. As the balance gas goes from pure N₂ to pure H₂, the fraction of HCN in the effluent decreases. Thus, increasing mol fraction of N₂ in the feed gas can be used to increase the selectivity for HCN. Similarly, if the feed gas composition is kept constant at 19% CH₄ and 81% N₂, then increasing the total pressure decreases the selectivity for HCN (Figure 4b). Thus, by tuning the composition of the feed gas by adjusting the relative amounts of H₂ and N₂, and by tuning the reaction pressure, the composition of the effluent can be

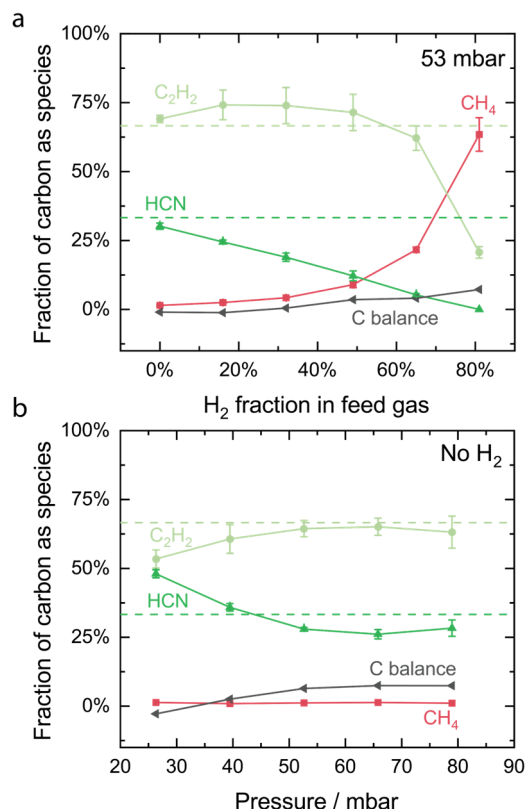
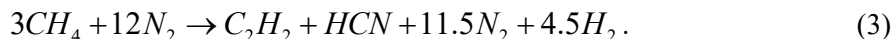


Figure 4. Trends in plasma effluent composition with (a) H₂ fraction in the plasma feed gas and (b) pressure. In both panels, the total flow rate to the plasma was 420 SCCM and the RF power was 450 W. The CH₄ mol fraction in the feed was constant at 19% for both panels. In (a), N₂ made up the balance that was not H₂ or CH₄. The pressure was constant at 53 mbar. In (b), the feed gas composition was constant at 19% CH₄ and 81% N₂. Ethane and ethylene have been omitted for clarity. The dashed lines indicate the expected fractions of carbon as C₂H₂ (light green) and HCN (dark green) if the yield of C₂H₂ + HCN were 100%.

controlled. Elucidation of these trends will be the subject of a future publication. In this work we focus on proof of the overall process concept of the plasma-catalytic synthesis of AN from CH₄ and N₂.

Since it has come up in discussion, we address here the fact that the plasma step of this process operates under sub-ambient pressure. Operating a vacuum reactor has some disadvantages. For example, it requires passing the process gas through a pump, which increases capital expenditures, operating expenditures, and maintenance. However, for nonequilibrium plasma processes, the reaction kinetics can be orders of magnitude faster at low pressure even for similar specific energy input, which can compensate for higher volumetric flow rates at low pressure for a given molar flow rate. The result is that operating at reduced pressure can result in similar reactor volumetric productivity to operating at atmospheric pressure.¹⁶ Furthermore, if the chemistry is highly endothermic, such as the reaction discussed in this work, then the power required by the chemistry is typically greater than the power

required by the vacuum pump. For example, consider the synthesis of 1 mole of C_2H_2 and 1 mole of HCN from a feedstock that is 20% CH_4 balance N_2 :



The enthalpy change of this reaction at $T=298$ K is $\Delta H_{298} = 587 \text{ kJ mol}^{-1}$ of reaction, as written. This enthalpy change is the minimum electricity required, and any inefficiencies will increase the energy input required by the chemical reaction. All the gases in the effluent, C_2H_2 , HCN, N_2 and H_2 must be compressed after the plasma up to atmospheric pressure. The minimum work required to isothermally compress an ideal gas is:


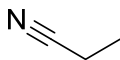
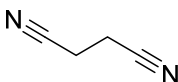
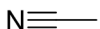
$$\dot{W}_{\text{pump}} = nRT \ln \left(\frac{P_2}{P_1} \right), \quad (4)$$

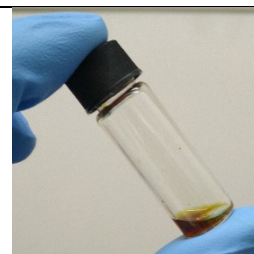
Where n is the number of mols of gas that must be compressed, which is 18 moles of gas for 1 mole of reaction (3) as written, R is the ideal gas constant, T is the temperature of the isothermal compression, P_2 is ambient pressure (1 bar) and P_1 is the plasma reactor pressure (0.05 bar). Assuming the gas is at 300 K, then approximately 134 kJ mol^{-1} of reaction (3) is required to compress the gas. Typical pump efficiencies are greater than 50%, thus we expect the electricity required by the pump to be in the range from 0.7 to 1.4 $\text{kWh kg}_{\text{AN}}^{-1}$. This pumping power requirement is much smaller than the specific energy requirements we have measured thus far (Figure 3). However, as the plasma reaction approaches its theoretical minimum value ($3.1 \text{ kWh kg}_{\text{AN}}^{-1}$), the work required by the pump can become a significant fraction of the electrical load, but it is still expected to be less than the work required by the plasma. There are also strategies that could be employed involving turbines to reversibly expand the feedstock to the plasma reactor pressure to recover some work to drive the vacuum pump, for example by connecting the turbine to the pump using a rotating shaft.

To prove the concept in Figure 1 of AN synthesis from $C_2H_2 + HCN$ intermediates, which in turn were synthesized from $CH_4 + N_2$ in a plasma, we performed several experiments passing the effluent of the plasma reactor through a packed bed of ZnO catalysts after bringing the gas up to ambient pressure. In all experiments reported herein, the catalyst bed was maintained at 500°C , which was found to provide the highest AN production rate in a quick screening of temperatures. Two different C_2H_2 :HCN ratios were examined to see the effect on the byproducts in the liquid. In the first experiment acetylene rich conditions were used at C_2H_2 :HCN = 2.5:1; and in the second experiment nominally stoichiometric conditions were used at C_2H_2 :HCN = 1.05:1. In both cases, the conversion in the catalytic bed of C_2H_2 was 100%, and HCN was greater than 80%. AN was a major product, but there were byproducts. The

compounds present in the liquid product, detected by GC-MS at a concentration greater than 10% of AN, are listed in Table 3 on a molar basis normalized to AN. In other words, the compounds listed in Table 3 were the most abundant compounds detected in the liquid.

Table 3. Major liquid products collected in the trap after the thermocatalytic reactor for two different ratios of C₂H₂ to HCN. The catalytic reaction temperature was 500 °C and the pressure was near ambient. All species concentrations have been normalized to the concentration of AN. Digital image is a picture of a small amount of the product liquid in a vial.

		Plasma effluent composition	
		2.5C ₂ H ₂ + HCN	1.05C ₂ H ₂ + HCN
Compound	Structure	Amount relative to AN (molar basis)	
Acrylonitrile (AN)		1.0	1.0
Benzene		1.13	0.069
Propanenitrile		---	1.70
Butanedinitrile		---	1.34
Acetonitrile		0.12	0.21
C ₂ H ₂ consumed in catalytic reactor:		100%	100%
HCN consumed in catalytic reactor:		100%	83.6%



The relative amount of acetylene to hydrogen cyanide had a significant effect on the impurities present in the liquid. For the C₂H₂-rich case, the only major impurity was benzene. In the nominally stoichiometric case, significant amounts of propanenitrile and butanedinitrile were detected with very little benzene. The result suggests that yield of AN may be enhanced at conditions that are slightly C₂H₂-rich. The abundance of propanenitrile indicates that for stoichiometric mixtures it may be advantageous to remove hydrogen before thermocatalytic AN synthesis; or that hydrogen tolerant catalysts are needed. However, these results are preliminary, and a more thorough characterization of the catalyst is required before drawing strong conclusions. For example, the effects of thermocatalytic reaction temperature, flow-normalized catalyst amount, C₂H₂:HCN ratio, and catalyst material could be systematically studied since these are all parameters that are straightforward to control. Ultimately it would be helpful to understand the catalytic mechanism so reaction engineering and scale-up design work can be performed more systematically. Work is ongoing in our laboratory towards these ends.

Moving to place this process concept in a broader context, the synthesis of AN from CH₄ and N₂ could produce value in several ways. First, it may be possible to produce AN from this route at a price that is competitive with the industrial state-of-the-art SOHIO process, which produces 90% of AN worldwide.¹⁷ The SOHIO process is based upon the ammoxidation of propylene to synthesize AN:



The ammonia is produced by the Haber-Bosch process, which consumes hydrogen that is produced by steam reforming of hydrocarbons. The hydrocarbon steam reforming produces CO₂. Second, it may be possible to produce AN by our plasma-catalytic process with less CO₂ emission when compared to the SOHIO process, effectively decarbonizing AN. To assess the feasibility of economic viability and potential for AN decarbonization, we performed some simple preliminary technoeconomic estimates.

The industrial state-of-the-art SOHIO process is the benchmark. The propylene used for the synthesis of AN by ammoxidation is produced by naphtha crackers.¹⁸ The process is energy and CO₂ intensive, requiring approximately 2.8 kWh per kg of propylene, and emitting 1.0 kg CO₂e per kg of propylene.¹⁸ Moreover, the propylene, which costs approximately \$1.0 kg⁻¹, comprises 67% of the cost of producing AN by ammoxidation,¹⁹ resulting in a production cost of approximately \$1.5 per kg of acrylonitrile. The ammonia used by the SOHIO process is made by the Haber-Bosch process using hydrogen that is assumed to be synthesized by methane steam reforming, which requires 9.4 kWh per kg of NH₃,²⁰ and emits approximately 1.5 kg CO₂e per kg NH₃.²¹ Considering small inefficiencies and waste in the process, 0.86 kg of propylene and 0.39 kg of ammonia are required to synthesize 1.0 kg of AN, resulting in the following process *performance metrics for ammoxidation*: 6.1 kWh per kg_{AN}, 1.4 kg CO₂e per kg_{AN}, and a production cost of \$1.5 per kg_{AN}.¹⁷ Recovery of heat at a high temperature is possible from the ammoxidation reaction because it is strongly exothermic, and estimates for the electricity and heat outputs have been made as 0.28 kWh and 0.91 kWh per kg_{AN} respectively.¹

In performing technoeconomic and lifecycle estimates for the nonequilibrium plasma-catalytic process, we made some assumptions to analyze what we believe to be the best-case feasible scenario based on the public literature. The electricity required by the plasma was taken as the main cost driver. Previous technoeconomic assessment of nonequilibrium plasma-chemical processes for similar endothermic reactions, operating at similar pressures, and with power supplies that have similar capital expenditure (CAPEX) requirements of approximately \$1 W⁻¹, have found that the total CAPEX and operating expenditures (OPEX), in \$ kg_{product}⁻¹, are approximately twice the cost of electricity used by the process.²² We therefore made TEA estimates by finding the specific energy requirement (SER) in units of

kWh kg_{AN}⁻¹, converting that SER to a \$_{elec} kg_{AN}⁻¹ of electricity, and then the cost to produce 1 kg of AN was taken as twice the electricity cost plus the cost of CH₄ and N₂ inputs.

We estimate, based on the public literature for plasma chemical processing, that the minimum specific energy requirement for the process illustrated in Figure 1 is approximately 5.6 kWh kg_{AN}⁻¹; and this number is the goal for future research. Acetylene synthesis from CH₄ provides an example that illustrates the enormous potential of nonequilibrium plasmas. For a process to synthesize C₂H₂ from CH₄ that is governed by local equilibrium, such as a thermal plasma, the entire gas must be heated to a temperature where the thermodynamics are favorable, and then the reaction enthalpy must be supplied. Following reaction, the products must be quenched. The theoretical minimum energy required per mass of C₂H₂ for a thermal process has been estimated to be 7.9 kWh kg_{C₂H₂}⁻¹ (Table 3).²³ The most energy-efficient thermal plasma processes for the synthesis of C₂H₂ from CH₄ have reported SER values of 9.0 kWh kg_{C₂H₂}⁻¹,²⁴ which is very close to the thermal limit. The literature on the use of nonequilibrium CH₄ plasmas for C₂H₂ synthesis is sparse, but early work on microwave plasmas operating at pressures near 0.1 bar reported SER values as low as 6.2 kWh kg_{C₂H₂}⁻¹,²⁵ less than the thermal limit. The ultimate thermodynamic limit for a nonequilibrium process operating at ambient temperature would be the reaction enthalpy of 4.0 kWh kg_{AN}⁻¹. This example of C₂H₂ synthesis from CH₄ demonstrates that it is feasible for nonequilibrium plasmas to have lower specific energy requirements than the theoretical lower limit for thermal plasmas. Assuming that some improvement could be made with systematic optimization, and that the HCN SER under this optimized condition is similar to acetylene, we set a goal that is expected to be feasible of 5.6 kWh kg_{AN}⁻¹ for nonequilibrium plasma-catalytic synthesis.

Using a specific energy input of 5.6 kWh kg_{AN}⁻¹, the assumption that all CAPEX and OPEX is twice the cost of electricity, plus the other inputs CH₄ and N₂, we made some simple economic estimates of the cost to produce one kilogram of acrylonitrile. The input parameter estimates were taken from market values late in the year 2022. There are several important conclusions to be drawn from the data in Table 4. First, at a small scale before saturation of the market for AN, which is approximately 6 million tons year⁻¹, 90% of the value produced by this plasma-catalytic process is in the AN. For each kg of AN that is produced, there is only 0.17 kg of H₂ produced as a byproduct. In Table 4, we have conservatively used as a value for H₂ the current United States Department of Energy goal for 2030 of 1 \$ kg_{H₂}⁻¹. However, this value is not very important, since the value of AN is also in the range 1 to 3 \$ kg_{AN}⁻¹; and thus the value of AN is approximately the same as H₂ per mass. The important point is that the plasma-catalytic process produces much less H₂ by mass, only 0.17 kg_{H₂} kg_{AN}⁻¹. Thus, approximately 90% of the value produced by the process is in the AN. The situation changes at larger scales greater than 10 million tons year⁻¹, but a discussion of that scenario is beyond the scope of this paper. Second, from Table 4, the plasma-catalytic process can be competitive with water electrolysis in the specific energy requirement of

the H₂ produced. More specifically, in this best case scenario, it is expected that the hydrogen will require 33 kWh kg_{H₂}⁻¹ to produce; which is similar to water electrolysis at an industrial scale that requires 55 kWh kg_{H₂}⁻¹ at 61% plant efficiency.⁴ Finally, the production cost of AN (\$1.35 kg_{AN}⁻¹), before sale or utilization of the H₂, is already competitive with the cost of production for the SOHIO process (\$1.5 kg_{AN}⁻¹

Table 4. Technoeconomic estimates of plasma-catalytic AN synthesis. (AN) Acrylonitrile and (SER) specific energy requirement.

Input parameter	Value	Units
CH ₄ consumed	0.91	kg _{CH₄} / kg _{AN}
N ₂ consumed	0.26	kg _{N₂} / kg _{AN}
AN produced	1	kg _{AN} / kg _{AN}
H ₂ produced	0.17	kg _{H₂} / kg _{AN}
HCN consumed	0.51	kg _{HCN} / kg _{AN}
C ₂ H ₂ consumed	0.49	kg _{C₂H₂} / kg _{AN}
Cost of natural gas (CH ₄)	0.47	\$ / kg _{CH₄}
Cost of N ₂	0.54	\$ / kg _{N₂}
Cost of electricity	0.07	\$ / kWh
CAPEX and other OPEX	0.07	\$ / kWh
Value of H ₂	1.0	\$ / kg _{H₂}
Nonequilibrium plasma-catalysis (best-case scenario)		
Gross SER of AN	5.6	kWh / kg _{AN}
Gross SER of H ₂	33	kWh / kg _{H₂}
Production cost	1.35	\$ / kg _{AN}
Production cost less H ₂ value	1.18	\$ / kg _{AN}

¹). Therefore, H₂ represents a profitable byproduct, or it can be oxidized to provide electricity for this energy intensive plasma-catalytic process. Compared to water electrolysis, this plasma-catalytic process is expected to have a similar electricity intensity per mass of H₂ produced at an industrial scale but be more profitable because AN is more valuable than O₂. However, research is necessary to close the gap between the actual performance (Figure 3) and the technical goal (Table 4). Once the specific energy requirement is less than 10 kWh kg_{AN}⁻¹, expenditure of the resources required to do a more rigorous and detailed technoeconomic analysis, including incorporation of actual product distributions, efficiencies of power transformers, cost of separation, sensitivity analysis and component breakdowns, etc. is justified.

In addition to the plasma-catalytic process being economically competitive with the SOHIO process in the best-case scenario, it also is expected to have lower CO₂ emissions thereby decarbonizing the production of AN. Even if the plasma process is driven by low carbon electricity, the production of methane still can result in CO₂ emission because that is a common impurity in the primary resource. Methane is mixed with CO₂ in biogas and natural gas. For biogas, the CO₂ is photosynthetic in origin, so its release to the atmosphere has an insignificant effect on the global CO₂ balance. However, for natural gas, we must consider the CO₂ emission associated with its removal from the hydrocarbon mixture that comes from beneath the surface of the earth, which results in approximately 0.37 kg_{CO_{2e}} kg_{CH₄}⁻¹. The

removal of this CO₂ also requires a small amount of energy, approximately 0.073 kWh kg_{CH₄}⁻¹.²⁶ Similarly, production of N₂ by air separation requires a small amount of energy, approximately 0.069 kWh kg_{N₂}⁻¹.²⁷ If this electricity to separate CH₄ and N₂ from the natural resource is supplied by the grid (0.39 kgCO_{2e} kWh⁻¹), and the electricity required to power the plasma is supplied from a low carbon source, such as wind (0.01 kgCO_{2e} kWh⁻¹), then the CO₂ emission of the proposed process (0.48 kgCO_{2e} kg_{AN}⁻¹) is much lower than state-of-the-art ammoxidation (1.4 kgCO_{2e} kg_{AN}⁻¹). The overall economic and CO₂ emission comparisons between the SOHIO process and the best-case plasma-catalytic process are presented in Table 5.

Table 5. CO_{2e} emission, energy cost and monetary cost for producing acrylonitrile (AN) normalized per kg of AN produced. Electricity produced from wind energy is assumed to power the plasma (0.01 kgCO_{2e} kWh⁻¹).

Method (per kg _{AN})	CO _{2e}	Gross energy	Gross cost
Ammoxidation (state-of-the-art)	1.4 kgCO _{2e}	6.1 kWh	\$1.50
Nonequilibrium plasma (best-case)	0.48 kgCO _{2e}	5.6 kWh	\$1.35

Conclusions.

In this work, we have demonstrated a proof-of-concept plasma-catalytic process to synthesize acrylonitrile (AN, CH₂CHCN) from methane (CH₄) and nitrogen (N₂). The process involves two steps that occur in direct fluid communication: 1) plasma synthesis of C₂H₂ + HCN intermediates from methane and nitrogen; and then 2) downstream thermocatalytic synthesis of AN from the acetylene and hydrogen cyanide intermediates. From the plasma step, methane conversion >90% and yield of C₂H₂+HCN > 90% was measured. The yield of C₂H₂+HCN increases with increasing throughput at constant specific energy input. Assuming perfect downstream catalytic conversion of C₂H₂ and HCN into AN, we measured an ideal specific energy requirement of AN of 73.1 kWh kg_{AN}⁻¹. Actual thermocatalytic experiments performed by passing the plasma effluent through a packed bed of ZnO catalyst at 500 °C revealed large amounts of acrylonitrile. When the plasma effluent was rich in C₂H₂ relative to HCN, the major impurity produced by the thermocatalytic reactor was benzene; and when it was nominally stoichiometric C₂H₂+HCN, the major impurities were propanenitrile and butanedinitrile. A best-case economic and lifecycle estimate was performed to set technical goals for further development of this plasma-catalytic process. At a specific energy requirement for AN of 5.6 kWh kg_{AN}⁻¹, the cost of production for AN is competitive with the industrial state-of-the-art SOHIO ammoxidation process. When driven by low CO_{2e} electricity, such as wind or nuclear power, the plasma-catalytic process produces dramatically less CO_{2e} kg_{AN}⁻¹ compared to SOHIO ammoxidation. The hydrogen produced by the plasma-catalytic process can either be sold at a profit or oxidized to produce electricity to be fed back into the plant during lulls in electricity supply.

Author contributions.

The plasma-catalytic process was developed by C. Page and E. Thimsen who have filed a provisional patent application for it. A. Peralta and C. Page carried out the experiments under the supervision of E. Thimsen who aided in design. A. Ponukumati and M. Foston did liquid product analysis. E. Thimsen drafted the manuscript. All authors contributed to it.

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Data availability statement.

The data that was used to generate the graphs in Figures 3 and 4 can be found in the supplementary material in Tables S1 and S2. The raw data from the throughput, balance gas and pressure experiments can be found in the supplementary material in tables S3 to S5. Error bars in Figures 3 and 4 were determined by triplicate experiments, which indicated the precision of the output data reported here is 10% of the value.

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References.

1. Baker RW, Lokhandwala K. Natural Gas Processing with Membranes: An Overview. *Ind. Eng. Chem. Res.* 2008;47:2109-2121.
2. Aghel B, Behaein S, Alobaid F. CO₂ capture from biogas by biomass-based adsorbents: A review. *Fuel.* 2022;328:125276.
3. Oni AO, Anaya K, Giwa T, Di Lullo G, Kumar A. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. *Energ Convers Manage.* 2022;254:115245.
4. Shaner MR, Atwater HA, Lewis NS, McFarland EW. A comparative technoeconomic analysis of renewable hydrogen production using solar energy. *Energ. Environ. Sci.* 2016;9:2354-2371.
5. Sarafranz MM, Tran NN, Nguyen H, et al. Tri-fold process integration leveraging high- and low-temperature plasmas: From biomass to fertilizers with local energy and for local use. *Journal of Advanced Manufacturing and Processing.* 2021;3:e10081.
6. Fulcheri L, Schwob Y. From methane to hydrogen, carbon black and water. *Int. J. Hydrog. Energy.* 1995;20:197-202.
7. Oldham T, Simon K, Ferriell DR, Belcher MA, Rubin A, Thimsen E. Highly Uniform Activation of Carbon Fiber Reinforced Thermoplastics by Low-Temperature Plasma. *ACS Applied Polymer Materials.* 2019;1:2638-2648.

8. Trots I-T, Zimmermann T, Schüth F. Catalytic Reactions of Acetylene: A Feedstock for the Chemical Industry Revisited. *Chem. Rev.* 2014;114:1761-1782.
9. Spence LRU, Park E, Butterbaugh DJ, Krocker EH, Inventors. PROCESS FOR THE PREPARATION OF ACRYLONITRILE. US patent 2,385,5511945.
10. Spaulding DC, Brockway CE, Inventors. METHOD FOR PREPARING ACRYLONITRILE BY VAPOR PHASE CATALYTIC REACTION OF ACETYLENE AND HYDROGEN CYANIDE. US patent 2,502,6781950.
11. Uner NB, Thimsen E. Low temperature plasma as a means to transform nanoparticle atomic structure. *Plasma Source. Sci. Technol.* 2018;27:074005.
12. Thimsen E. Entropy production and chemical reactions in nonequilibrium plasma. *AIChE J.* 2021;67:e17291.
13. Chen X, Thimsen E. Stationary states of hydrogen-producing reactions in nonequilibrium plasma. *AIChE J.* 2022:e17952.
14. Leutner HW. Production of Hydrogen Cyanide Using Plasma Jet. *Ind. Eng. Chem. Process. Design Dev.* 1963;2:315-318.
15. Henderson L, Shukla P, Rudolph V, Duckworth G. Production of Cyanide Using Thermal Plasma: Thermodynamic Analysis and Process-Specific Energy Consumption. *Ind. Eng. Chem. Res.* 2020;59:21347-21358.
16. Uner NB, Thimsen E. Superlocal chemical reaction equilibrium in low temperature plasma. *AIChE J.* 2020;66:e16948.
17. Cespi D, Passarini F, Neri E, Vassura I, Ciacci L, Cavani F. Life Cycle Assessment comparison of two ways for acrylonitrile production: the SOHIO process and an alternative route using propane. *Journal of Cleaner Production.* 2014;69:17-25.
18. Müller RC, Schiessl A, Volk R, Schultmann F. Assessment of site-specific greenhouse gas emissions of chemical producers: Case studies of propylene and toluene diisocyanate. *Journal of Cleaner Production.* 2021;317:128086.
19. Brazdil JF. Strategies for the selective catalytic oxidation of alkanes. *Topics in Catalysis.* 2006;38:289-294.
20. Bicer Y, Dincer I, Zamfirescu C, Vezina G, Raso F. Comparative life cycle assessment of various ammonia production methods. *Journal of Cleaner Production.* 2016;135:1379-1395.
21. Smith C, Hill AK, Torrente-Murciano L. Current and future role of Haber–Bosch ammonia in a carbon-free energy landscape. *Energ. Environ. Sci.* 2020;13:331-344.
22. van Rooij GJ, Akse HN, Bongers WA, van de Sanden MCM. Plasma for electrification of chemical industry: a case study on CO₂ reduction. *Plasma. Phys. Control. Fusion.* 2017;60:014019.
23. Anderson RP, Fincke JR, Taylor CE. Conversion of natural gas to liquids via acetylene as an intermediate. *Fuel.* 2002;81:909-925.
24. Fincke JR, Anderson RP, Hyde T, et al. Plasma Thermal Conversion of Methane to Acetylene. *Plasma Chem. Plasma Process.* 2002;22:105-136.
25. Fridman AA, Babaritskiy AI, Givotov VK, Dyomkin SA, Nester SA, Rusanov VD. Methane Conversion in Acetylene in the Nonequilibrium MCW-Discharge. Paper presented at: Tenth International Symposium on Plasma Chemistry 1991; Bochum.
26. Rochelle GT. Amine Scrubbing for CO₂ Capture. *Science.* 2009;325:1652-1654.
27. Gopan A, Kumfer BM, Phillips J, Thimsen D, Smith R, Axelbaum RL. Process design and performance analysis of a Staged, Pressurized Oxy-Combustion (SPOC) power plant for carbon capture. *Applied Energy.* 2014;125:179-188.