

ISOTOPIC EXPERIMENTAL AND MODELLING STUDY OF ACETYLENE FORMATION IN A PLASMA REACTOR USING AN A.C CORONA DISCHARGE

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Abstract

The mechanism of C_2 formation in methane conversion using plasma discharge has been studied by researchers around the world with ambiguous conclusions. Motivated by this challenge, this paper discusses the pathway of acetylene formation based on experimental results using deuterium isotope. Methane was fed with deuterium with a ratio of 1 to 5. Ethane and acetylene were also fed with deuterium at the same ratio (1 to 5) to study the composition of acetylene products. Experimental results suggest that ethane, C_2H_6 , was formed from the coupling of CH_3 radicals; C_2H_4 was formed from the coupling of CH_2 or CH and CH_4 ; C_2H_2 formed involving C and C_2 radicals. Secondary dehydrogenation may also account for some production of ethylene and acetylene from ethane and ethylene, respectively, and is insignificant compared to the radical coupling mechanism. A modeling study was done to try comparing and explaining the experimental work, particularly in C_2 selectivity and acetylene formation. C_2 selectivity of methane conversion by non-thermal plasma has been found to be a function of the specific power input. At low power, ethane is the major product; while at high power, acetylene is mainly produced. However, in some cases even at low specific energy input (low temperature) and low electron density such as corona discharge, acetylene is still the main product. There are two parts of the model: plasma physics and free radical chemistry, the results showed that all C_2 products are produced simultaneously from $CH_x(x=0-3)$ radical's reactions at low temperature. The free radical distribution created initially from direct methane electron impact reactions depends on the applied reduced electric field strength (E/N): CH_3 radicals are the most abundant species at low E/N while C , CH , CH_2 radicals are present at high E/N (precursors of C_2 radicals).

Part I: Isotopic Study of Acetylene Formation

Introduction

Natural gas has been considered a bridge energy source from fossil to non-fossil into the hydrogen economy. Methane conversion using cold plasma discharge has been under investigation by many scholars around the world¹⁻⁶. In a plasma discharge, methane can be converted into many useful products such as hydrogen and C₂ hydrocarbons, including acetylene, ethylene and ethane. The advantage of low temperature plasma methane conversion is that the products are not limited by thermodynamics indicating that a non-equilibrium composition of products can be obtained. The controlling factors, however, are the electrical parameters such as electric field, electron density and power consumption. Manipulating these factors might lead to better optimization of the system and control toward the desired products, for example hydrogen and ethylene.

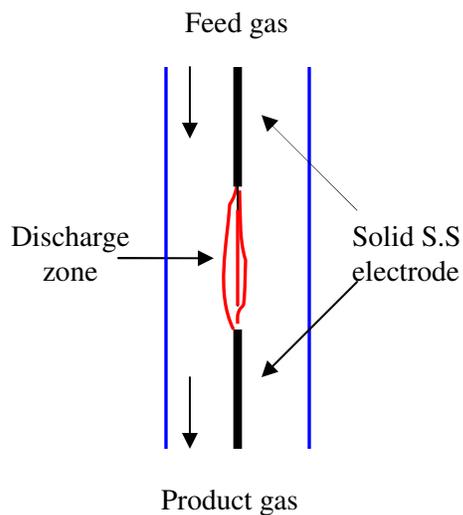
The objective of this work is to have a better understanding of C₂ formation pathway by studying the formation of acetylene that is the predominant C₂ product observed in corona discharge. This is a building block that will further help understanding other product formation mechanisms when oxygen species such as steam, carbon dioxide and oxygen are present. The goal is to control the pathways to get the desired products with yields as high as possible and with low power consumption.

In this paper, a deuterium isotope (D₂) was used as a reactant fed with methane to trace the products and study their compositions from which the pathways of C₂ formation can be determined. By deconvoluting the mass spectroscopic signals obtained from the product gas, the composition of the deuterated species was calculated, and its contribution to the underlying pathway revealed.

Experimental

The reactor configuration is point-to-point with two electrodes placed vertically in a 10 mm-ID quartz tube. The gap between the electrodes is 5 mm. Discharge occurs between this gas gap when a sufficiently high voltage (2-5 kV) is applied to the system. The reactor configuration is summarized in Figure 1. Feed gas includes methane 99.9% (AirGas) and deuterium 99.6% pure (0.4% HD from Cambridge Isotope Laboratories, Inc.) Typical methane conversions and selectivities are shown in Table 1.

The power supply system includes an Elgar AC power supply model 251B, a Wavetek model 182A waveform generator, and a midpoint grounded Magnetec Jefferson high voltage transformer. The low side voltage is in a range of 40V-100V. Frequency can be varied from 100 Hz to 600 Hz; for this study the operating frequency is 300 Hz. The power analyzer includes a Tektronics TDS 754 oscilloscope, an A622 current probe and a P6139A voltage probe. Further experimental details have been described elsewhere¹⁸



Flowrate (sccm)	30	60	90	180
Methane Conversion	24.8	16.8	13.6	8.6
Hydrogen Selectivity	66.9	61.5	59.7	61.7
Hydrogen Yield	16.6	10.3	8.1	5.3
Acetylene Selectivity	44.7	43.2	45.2	48.2
Acetylene Yield	11.1	7.2	6.1	4.1
Ethylene Selectivity	11.1	11.1	10.8	9.1
Ethylene Yield	2.7	1.9	1.5	0.8
Ethane Selectivity	16.6	18.5	19.0	20.1
Ethane Yield	4.1	3.1	2.6	1.7
C2 Yield	17.9	12.2	10.2	6.6
Carbon Balance	72.3	72.8	75.0	77.3
Hydrogen Balance	96.0	91.7	90.6	93.3
eV/mol CH ₄ converted	87.9	59.6	52.7	44.9

Figure 1: Reactor configuration point-to-point with tubular reaction inside quartz wall

Table 1: Experiments of CH₄ and D₂ ratio 1:5 at 300 Hz, 5mm gas gap, 10 mm ID varying residence time

An MKS mass spectroscopy (MS) system model QMG 420 was used for the isotopic study. The product gas was analyzed with the MKS Quadruple Residual Gas Analyzer. The bulk chamber and vacuum pumps are from a preexisting Balzer's unit. The data is analyzed using the PPT software package by MKS. The closed system pressure is 10^{-7} Torr, while the operating pressure is desired to be in 10^{-6} - 10^{-5} Torr. The mass spectrometer is connected after the Gas Chromatograph Carle Series 400 AGC, Model 04157 with a thermal conductivity detector, an HTS system for hydrogen separation and analysis.

Results and Discussion

Methyl radical formation:

Experiments with methane and excess deuterium (ratio 1:5) as the feed were carried out and the MS signals of methane in the products were deconvoluted to show the isotopic distribution/composition. Methane compositions show about 90% CH₄ and about 10% isotopically substituted methane, the compositions of the methane isotopes are slightly higher in the order CH₃D > CH₂D₂ > CHD₃ > CD₄ (Figure 2). This suggests that experimentally, the probability of formation of the radicals CH₃, CH₂, CH and C is in agreement with Hoang's calculations¹², and Kado and Nozaki's work^{4,7} where their concentrations are in the same order of magnitude for a corona discharge.

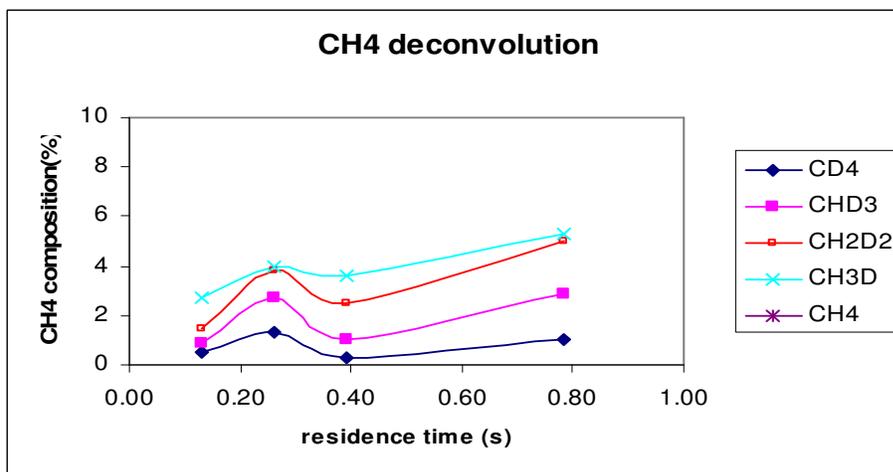


Figure 2: Methane composition after the reaction with methane to D₂ ratio 1:5 at 300 Hz 10-mm ID reactor

The data for acetylene and its isotopes from these experiments are shown in Figure 3. The deconvolution finds that the composition includes C₂H₂, C₂HD and C₂D₂. With a feed ratio of 5 to 1 of D₂ to CH₄, the primary isotope of the acetylene species that is observed is C₂D₂. The composition of acetylene itself, C₂H₂, is very low compared to C₂D₂ and also C₂HD. Also in Figure 3, it may be seen that as residence time increases, the C₂D₂ composition decreases while C₂HD and C₂H₂ compositions increase. This happens because at high residence time, more methane is converted and more hydrogen (H) is produced from that conversion (Table 1). More hydrogen can facilitate the incorporation of H into acetylene species either by CH coupling or C₂ abstracting H. The increase in C₂HD composition may be due to higher CH radical composition and CH coupling with CD to form C₂HD. Higher CH results from the initial electron impact and also from C abstracting H.

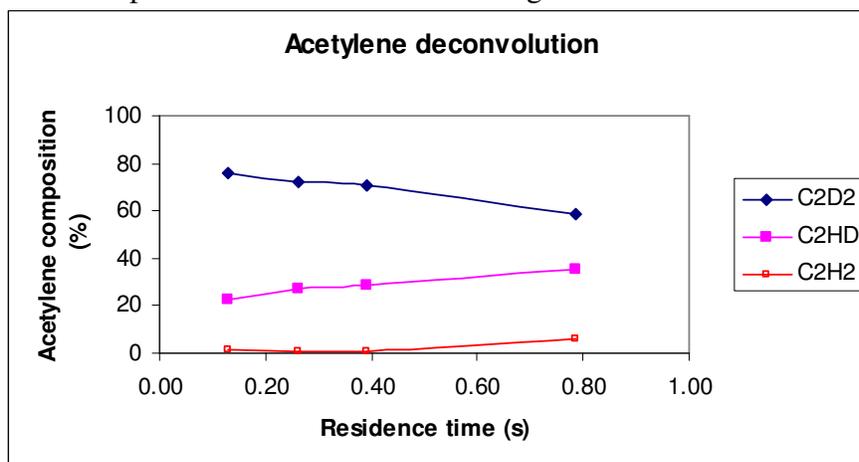


Figure 3: Acetylene composition from 5:1 D₂: CH₄ experiment at 300 Hz, 5mm gg, 10 mm ID reactor.

An argument may be made that the high composition of C₂D₂ is just due to scrambling effects of high amounts of D₂ with C₂H₂ in the products. To check the scrambling effect of deuterium, acetylene C₂H₂ was fed with D₂ with a ratio of 1 to 5

(C₂H₂: D₂) and the composition of the product gas was analyzed after the plasma was turned on. The experiment was repeated with varying total flowrates to give different residence times but keeping the same ratio of acetylene and deuterium. The results in Figure 4 show that C₂D₂ is lowest in composition compared to C₂H₂ and C₂HD. The total composition of the latter two components is less than 20% while composition of C₂H₂ stays above 80% and C₂HD:C₂D₂ ratio >1 with C₂HD being the primary (first) scrambling product. These results suggest that the extent of deuterium exchange is very low.

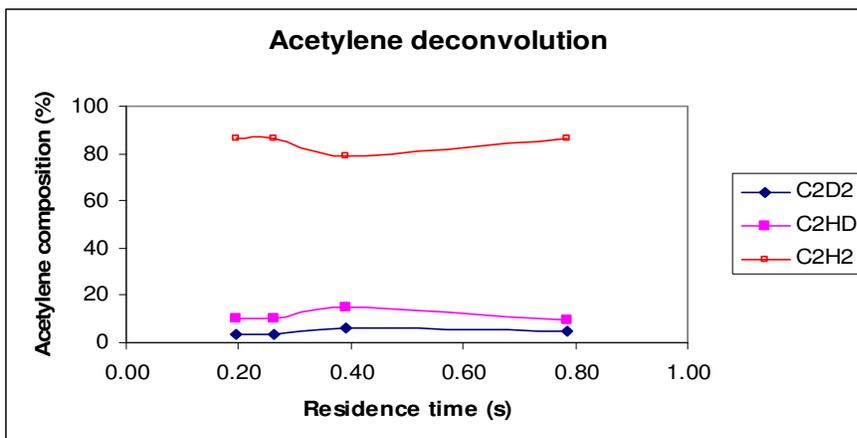


Figure 4: Acetylene and D₂ experiment with 1: 5 ratio varying residence time at 300 Hz 10 mm ID

As previously discussed, the high C₂D₂ composition among acetylene species is not due to scrambling effect. The formation of C₂D₂ must be due to one or more of the following pathways:

- (a) C₂D₄ → C₂D₂
- (b) C + CD₃ → C₂D₃; C₂D₃ + D → C₂D₂ + D₂ (Hoang's model¹²)
- (c) CD + CD → C₂D₂ (CD coupling)
- (d) C + C → C₂; C₂ + D → C₂D; C₂D + D → C₂D₂ (C₂D₂ via C and C₂ radicals)

The objective is then to develop an understanding of the dominant pathways for acetylene and C₂ formation by examining the production of the primary isotopic C₂ products.

a. Dehydrogenation:

In order to study the formation of acetylene from dehydrogenation of ethane, an experiment with ethane and deuterium (ratio 1:5) was carried out to determine the acetylene isotope distribution compared to the methane with deuterium experiments. The results show that the major composition is C₂D₂ and C₂HD with about equal probability, and the composition of C₂H₂ is much lower, seen in Figure 5. If dehydrogenation of ethane to acetylene is the major route, the highest acetylene composition must be C₂H₂, and not C₂D₂ or C₂HD. The observed acetylene composition suggests that ethane must dissociate into CH or C radicals by electron impact; these radicals, then abstract the dominant D to form C₂D₂ and C₂HD. The similar composition of C₂D₂ and C₂HD may be due to the competing reactions that

include C₂ abstracting D and CD coupling with CH. The rate constants for both reactions are in the same order of magnitude according to the NIST kinetics database¹⁵. Thus, the decomposition and radical combination pathway, rather than dehydrogenation, is the major route for forming acetylene from ethane. Also in these experiments, the methane selectivity is higher than acetylene selectivity. So the breakage of C-C bond produces substantial formation of methane by CH₃ recombination with H or D radicals and also confirms C-C bond cleavage.

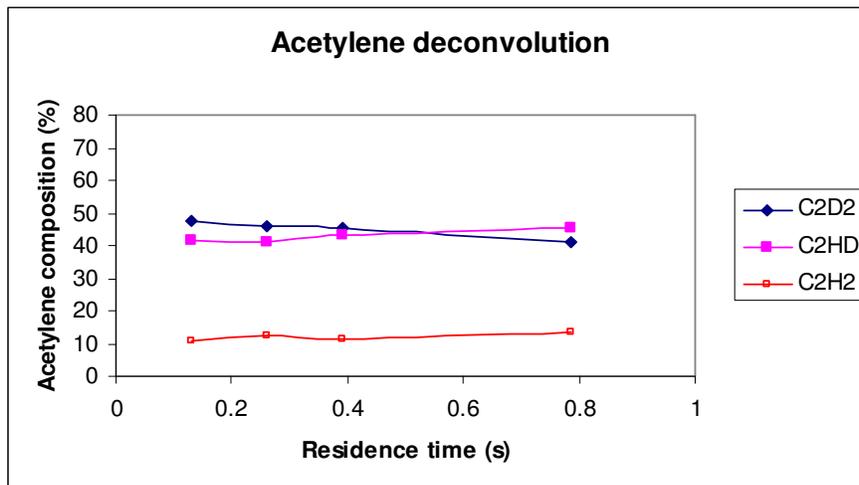


Figure 5: Acetylene deconvolution for ethane and deuterium ratio 1:5 at 300 Hz 10-mm ID

b. C + CH₃ combination:

Recent modeling results using a published hydrocarbon radical reaction mechanism (Hoang¹²) suggest that a major pathway is the coupling of C and CH₃ radicals. Forming C₂D₂ by this pathway would require the coupling of C and CD₃ radicals:



Hoang's results¹², however, are not consistent with the high composition of C₂D₂ observed since it would require substantial CD₃ radicals. Figure 3 shows the deconvoluted methane composition from the methane conversion experiments. The CD₄ composition, formed from CD₃+D, is indicative of the relative amount of CD₃ radicals and is relatively small compared to the more abundant isotopes including CH₃D. Acetylene formed via the pathway suggested by Hoang, with CH₃ as the dominant inferred methyl isotope, would form C₂H₂.

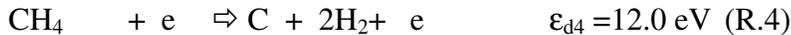
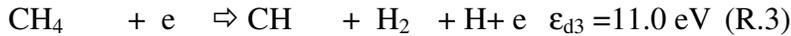
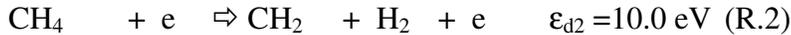
This leaves two possible routes (c and d) forming C₂D₂: the route from CD radical coupling and the route from C and C₂ radicals. The reaction rate constants for both are obtained from the NIST database¹⁵. The data suggest that these two routes may co-exist and compete to form C₂D₂ with comparable rates. Further discussions and conclusions can be referred to the presentation.

Part II: Modeling Study of C₂ Production Pathways

Conversion of methane to higher value commodities such as acetylene, ethylene, or hydrogen is of interest for monetizing some natural gas reserves. Low temperature plasmas have been found to have potential for smaller scale conversion processes. However, products of natural gas conversion are a mixture of ethane, ethylene, and acetylene. Ethane is non-reactive and primary used as a cracking feed, thus, low market value. Although both ethylene and acetylene are used as chemical feedstocks, ethylene is in much higher demand for polyolefin production and can be oligomerized to make fuels. Acetylene processes have disappeared primarily due to safety issue. Thus, control of selectivity to minimize ethane or maximize desirable ethylene remains to be achieved.

C₂ selectivity from methane conversion by non-thermal plasmas has been found to be a function of the specific power input. Ethane is the main product at low power and acetylene is the main product at high power. However, in some cases, at low specific energy input (low temperature) and low electron density such as in a corona discharge, acetylene is the main product, with some disagreement on the proposed pathways.

The objective of this work is to understand the pathways controlling C₂ selectivities through the development of a two part model: plasma physics and free radical chemistry. The plasma physics model solves the Boltzmann equation for the electron energies as a function of reactor geometry and reduced electric field by ELENDIF¹⁹. The reaction rate constants for electron impact reactions with methane are then obtained and calculation of rates of production of CH_x radicals made.



where ϵ_d is threshold energy for the dissociation processes

A free radical chemistry model based on the GRI combustion mechanism²⁰ is used to compute the C₂ pathways (Table 2). The results show that all C₂ products are produced simultaneously from CH_{x(x=0-3)} radical reactions at low temperature. The free radical distribution is created initially from direct methane electron impact reactions that depend on the reduced electric field (E/N): CH₃ radicals are the most abundant species at low E/N while C, CH, CH₂ radicals (precursors of C₂ radicals²¹) are prevalent at high E/N. High electric field operation (eg. 600Td) (small gas gap and sharp tip electrode) give a higher concentration of energetic electrons and reduce the wasted energy from vibrational excitation. The results of C₂ selectivities from the

Table 2 – The important reactions in plasma chemistry model - rate coefficient in form $k = A \times (T)^b \times \text{EXP}(-E/RT)$

REACTIONS		A(cm ³ /mol/s)	b	E (cal/mol)
Reaction involved with CH_{x(x=0-3)}, H radicals			[ref]	
1	2H + M ⇌ H ₂ + M	1.00E+18	-1.0	0
2	2H + H ₂ ⇌ 2H ₂	9.00E+16	-0.6	0
3	H+CH ⇌ C + H ₂	1.65E+14	0	0
4	H+CH ₂ (+M) ⇌ CH ₃ (+M)	6.00E+14	0	0
5	H + CH ₂ (S) ⇌ CH + H ₂	3.00E+13	0	0
6	H+CH ₃ (+M) ⇌ CH ₄ (+M)	1.39E+16	-0.5	536
7	H+CH ₄ ⇌ CH ₃ + H ₂	6.60E+08	1.6	10840
8	H+C ₂ H (+M) ⇌ C ₂ H ₂ (+M)	1.00E+17	-1.0	0
9	H+C ₂ H ₂ (+M) ⇌ C ₂ H ₃ (+M)	5.60E+12	0	2400
10	H+C ₂ H ₃ (+M) ⇌ C ₂ H ₄ (+M)	6.08E+12	0.3	280
11	H+C ₂ H ₃ ⇌ H ₂ + C ₂ H ₂	3.00E+13	0	0
12	H+C ₂ H ₄ (+M) ⇌ C ₂ H ₅ (+M)	5.40E+11	0.5	1820
13	H+C ₂ H ₄ ⇌ C ₂ H ₃ + H ₂	1.32E+06	2.5	12240
14	H+C ₂ H ₅ (+M) ⇌ C ₂ H ₆ (+M)	5.21E+17	-1.0	1580
15	H+C ₂ H ₅ ⇌ H ₂ + C ₂ H ₄	2.00E+12	0	0
16	H+C ₂ H ₆ ⇌ C ₂ H ₅ + H ₂	1.15E+08	1.9	7530
17	C+CH ₂ ⇌ H + C ₂ H	5.00E+13	0	0
18	C+CH ₃ ⇌ H + C ₂ H ₂	5.00E+13	0	0
19	CH+H ₂ ⇌ H + CH ₂	1.08E+14	0	3110
20	CH+CH ₂ ⇌ H + C ₂ H ₂	4.00E+13	0	0
21	CH+CH ₃ ⇌ H + C ₂ H ₃	3.00E+13	0	0
22	CH+CH ₄ ⇌ H + C ₂ H ₄	6.00E+13	0	0
23	CH ₂ + H ₂ ⇌ H + CH ₃	5.00E+05	2	7230
24	2CH ₂ ⇌ H ₂ + C ₂ H ₂	1.60E+15	0	11944
25	CH ₂ + CH ₃ ⇌ H + C ₂ H ₄	4.00E+13	0	0
26	CH ₂ + CH ₄ ⇌ 2CH ₃	2.46E+06	2	8270
27	CH ₂ (S)+H ₂ ⇌ CH ₃ + H	7.00E+13	0	0
28	CH ₂ (S)+CH ₃ ⇌ H + C ₂ H ₄	1.20E+13	0	-570
29	CH ₂ (S)+CH ₄ ⇌ 2CH ₃	1.60E+13	0	-570
30	CH ₂ (S)+C ₂ H ₆ ⇌ CH ₃ + C ₂ H ₅	4.00E+13	0	-550
31	2CH ₃ (+M) ⇌ C ₂ H ₆ (+M)	6.77E+16	-1.2	654
32	2CH ₃ ⇌ H + C ₂ H ₅	6.84E+12	0.1	10600
33	CH ₃ + C ₂ H ₄ ⇌ C ₂ H ₃ +CH ₄	2.27E+05	2	9200
34	CH ₃ + C ₂ H ₆ ⇌ C ₂ H ₅ + CH ₄	6.14E+06	1.7	10450
35	C ₂ H + H ₂ ⇌ H + C ₂ H ₂	5.68E+10	0.9	1993
36	C ₂ H ₄ (+M) ⇌ H ₂ +C ₂ H ₂ (+M)	8.00E+12	0.4	86770
37	CH+ H ₂ (+M) ⇌ CH ₃ (+M)	1.97E+12	0.4	-370
38	CH ₂ + CH ₂ ⇌ 2H + C ₂ H ₂	2.00E+14	0	10989
39	CH + CH ⇌ C ₂ H ₂	5.00E+13	0	0

Reactions involved with C₂ radicals [3]

40	C ₂ +H ₂	⇌C ₂ H+H	4.00E+5	2.4	1000
41	CH+CH	⇌C ₂ +H ₂	5.00E+12	0	0
42	C+C+M	⇌C ₂ +M	3.00E+14	0	-1000
43	C+CH	⇌C ₂ +H	5.00E+13	0	0
44	C+CH ₂	⇌C ₂ +H ₂	2.40E+12	0	980

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