# CHEMICAL REACTIONS IN PLASMAS. I. CONVERSION OF $C_1 - C_2$ HYDROCARBONS IN A HYDROGEN PLASMA JET – QUALITATIVE ASPECTS

By

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Atoms and molecules of gases or vapours can be dissociated into electrons and ions by high energy electron impact; the resulting mixture of charged and uncharged particles is called plasma, a term first used by LANGMUIR in 1929 [1]. The properties of different plasmas, the uses of plasmas for different chemica and nonchemical uses are well covered in literature [2, 3, 4, 5].

The plasma state of matter can be attained in many different ways: electric glow, corona and arc discharges, high energy radiation, high frequency and microwave excitation, etc. For chemical studies low pressure high frequency and microwave apparatus are often used, for technical purposes, however, higher pressure arc plasmas at higher temperatures are studied.

The electrically charged particles present in the plasma gas make it a conductor, and if placed in an electric field, heating occurs by Joule effect, imparting the gas high temperatures in the range of several  $10^3$  to  $10^4$  °K so that molecules dissociate into atoms and more complex radicals. The energy release upon recombination of these species can be used as an extremely intensive heat source permitting to carry out chemical reactions of endothermic character or alternatively, using the dissociated plasma gas as a reactant, the high reactivity of the free radicals formed can be made use of to produce new chemical compounds—impossible to synthetize by other means.

The most convenient device for producing a steady state plasma flow up to about 100 atm. pressure is the direct current plasma jet invented by GAGE [6], consisting of a hollow cone-shaped anode and a solid cathode with the gas to be ionized and heated flowing in the annular space between the electrodes. The high-enthalpy and electrically neutral plasma emerges from the anode orifice very much like a flame of an oxy-acetylene torch, into which reactants can be fed by means of suitable mixing slots.

With chemical reactions having a more favourable thermodynamic equilibrium composition at higher temperatures, very fast quenching of the reaction products is necessary in order to freeze reactions. Quenching can be effected by injecting additional cold reactant, either liquids or gases, by using a fluidized bed of cold particles or by expanding the reaction products to low pressure. With small scale plasma generators reaction product streams issuing from the anode nozzle can be cooled down abruptly through backmixing caused by jet action and expansion in a wide container.

Hydrocarbons, such as methane, can be converted into acetylene in a hydrogen plasma using the latter as heat source, and by quenching the effluent to temperatures where further chemical reactions are stopped. On this principle, large scale industrial production of acetylene was introduced in the sixties in Germany and in the USA [7, 8].

Feeding methane into a plasma jet of hydrogen yields, additionally to acetylene hydrogen, methane, ethane, ethylene, propane, propylene and different  $C_4$ -hydrocarbons, with a small amount of carbon formation being reported, according to the following overall equations:

acetylene:	$2 \operatorname{CH}_4  ightarrow \operatorname{C_2H}_2 + 3 \operatorname{H}_2$	
ethylene:	$2 \operatorname{CH}_4  ightarrow \operatorname{C}_2 \operatorname{H}_4 + 2 \operatorname{H}_2$	
ethane:	$2 \operatorname{CH}_4  ightarrow \operatorname{C}_2 \operatorname{H}_6 + \operatorname{H}_2$	
propane:	$3 \text{ CH}_4 \rightarrow \text{C}_3\text{H}_8 + 2 \text{ H}_2$	
propylene:	$3 \operatorname{CH}_4 \rightarrow \operatorname{C_3H_6} + 3 \operatorname{H_2}$	
methylacetylene:	$3 \text{ CH}_4 \rightarrow \text{C}_3\text{H}_4 + 4 \text{ H}_2$	
butanes:	$4 \text{ CH}_4 \rightarrow \text{iso} + n - \text{C}_4\text{H}_{10} + 3 \text{ H}_2$	etc.

The reaction paths leading to these compounds as described by different authors are contradictory, therefore a study was undertaken to throw more light on the reactions of the individual hydrocarbons found in the reaction products starting from methane, and on the interaction of hydrogen. In this first article the qualitative aspects are discussed.

#### Experimental

A micro plasma generator was used, consisting of a cone-shape copper anode nozzle with a tungsten cathode in the anode axis, both being watercooled. The electrodes were contained in a gas-tight housing. The reaction products emerging from the anode orifice were quenched by backmixing in a water-cooled glass compartment. Samples were led to a train of eight sample bottles separated by glass stopcocks and provided with sampling septa. Volumes of cooling water streams to the electrodes were measured by separate rotameters. Cooling water inlet and outlet temperatures were measured with mercury thermometers during each run.

Hydrogen was taken from a pressure cylinder through a two-stage pressure reducing valve. Hydrogen flow was measured by means of a rotameter.

38

Hydrocarbon reactant gases from pressure cylinders came through twostep pressure reducing valves and were measured by rotameters before being mixed to the hydrogen.

The power source consisted of a 6-way diode rectifier with several groups of resistors. The latter could be switched into different arrangements for power control. Power to the electrodes could be varied stepwise up to 2 kW. The arc was initiated by a high-frequency spark. The scheme of the experimental apparatus is depicted in Figs. 1 and 2.



Fig. 1. Electric power source

Hydrogen, methane, ethane, ethylene and acetylene were better than 99.6% purity. Products were analyzed by gas chromatography on an isothermal column containing GSC-120 packing with a flame ionization detector. Peak areas were determined from the chromatogram as a product of peak height and half-width. Methane, ethane, ethylene, acetylene, propane and propylene were resolved individually, whereas  $C_4$ -hydrocarbons gave one peak.

Experimental runs were started first by flushing the whole setup with nitrogen, then switching to hydrogen. Cooling water rates were set to desired values, and the arc was struck. With power adjusted to the desired value the hydrocarbon flow was set. After steady state set in the reaction mixture was led to sample flask No. 1: then, after setting new parameters, the new sample was led to the second sample flask, etc. During sampling all parameters were recorded.



Fig. 2. Plasma jet read

Net heat contained in the plasma was calculated by subtracting heat losses in cooling water streams from electric power applied to the plasma generator. Effects of heat of reactions and of hydrocarbons mixed to the hydrogen were neglected because of the small hydrocarbon concentrations used.

Individual runs were evaluated with a Hewlett-Packard calculator, Type 9100 B with magnetic card operated programs.

#### Experiments

Methane, ethane, ethylene and acetylene were fed separately into hydrogen entering the plasma generator. Feed rates were varied as follows:

nydrogen	35	to	78	gmoles	$\mathbf{per}$	hour	
1ydrocarbon	0.2	to	1.1	$\mathbf{gmoles}$	$\mathbf{per}$	$\mathbf{hour}$	

each at three different levels. Net plasma power was varied at three levels in the range of 400 to 1800 kcals/hour.

Net plasma power was divided by moles of hydrogen plus hydrocarbon to obtain specific plasma enthalpy in kcalories per gmole, with ambient temperature as basis.

Tables I-IV. contain hydrocarbon and hydrogen rates, net plasma enthalpy, hydrogen to carbon ratio, conversion values of hydrocarbons injected and selectivities for the hydrocarbons formed, the latter two on a  $C_1$ -basis, evaluated from gas chromatography analysis of effluents.

No attempt was made to assign plasma temperatures, because the size of the plasma "flame" was only of a few millimeters preventing determination of temperature distribution by spectroscopy and temperatures for atmospheric plasma hydrogen read from charts of enthalpy vs. temperature might be in gross error because of effects of dissociating hydrocarbons.

#### Methane

Selectivity data from Table I show selectivities within a set of constant hydrogen feed rate to converge for increasing plasma enthalpy. At low enthalpy levels acetylene is the main product, ethane is formed to a lesser extent and formation of  $C_{3+}$  hydrocarbons is relatively high.

Ethylene formation tends to zero. Increasing plasma enthalpy produces a relatively asymptotic concentration of ethylene, sharply decreases ethane and higher hydrocarbon formation and at the expense of the former compounds, enhances acetylene formation. Increasing hydrogen to carbon ratio decreases acetylene as well as ethylene formation and promotes that of ethane. At shorter contact times more ethane is formed with ethylene production hardly affected.

#### Ethane

Data are summarized in Table II. At constant residence time the lower the hydrogen to carbon ratio the higher the ratio of acetylene formed. The amount of ethylene increases too with decreasing H/C ratio, whereas that of methane increases. The amount of acetylene increases, and that of methane decreases sharply with residence time, indicating that the system under investigation is far from being at equilibrium. Formation of high molecular weight compounds is favoured at low plasma enthalpies.

#### Ethylene

Experimental data from Table III show that at low enthalpies acetylene and ethane are the main decomposition products along with small amounts of higher boiling hydrocarbons. With increasing plasma enthalpy, methane as secondary product appears with a pronounced maximum, after which ethane and higher hydrocarbons tend to zero whereas acetylene becomes again the main product. Increasing hydrogen to carbon ratio considerably increases methane selectivity, the same effect being observed with increasing contact times.

Table IMethane experiments

						na Conversion Selectivity (C,-basis) % to							
Run	F	eed, moles	s/hr	H/C	Plasma enthalpy	Conversion C <sub>1</sub> -basis	Selectivity (C <sub>1</sub> -basis) % to						
	H,	СН,	total	Tatio	kcal/mole	%	C <sub>2</sub> H <sub>6</sub>	C,H,	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>6</sub>	C₄	
101	35.0	0.22	35.22	316	12.8	12	20.3	8.1	64.2	3.6	0	3.6	
102	35.0	0.63	35.63	116	11.6	17	13.2	5.8	77.5	1.8	0.4	0.7	
103	35.0	1.08	36.08	69	12.9	21	6.4	6.3	82.8	1.2	0.9	0.5	
104	53.9	0.22	54.11	485	9.8	3	53.0	4.1	34.1	8.1	0	12.8	
105	53.9	0.63	54.53	176	11.8	10	16.0	7.8	69.9	2.7	0.3	2.0	
106	53.9	1.08	54.98	104	13.2	14	8.8	6.7	80.0	2.1	0.7	1.1	
107	77.8	0.22	78.02	698	4.5	3	65.5	6.5	11.0	5.8	0	13.0	
108	77.8	0.63	78.43	252	5.1	6	37.5	4.2	49.3	4.4	0	4.3	
109	77.8	1.08	78.88	149	5.0	7	17.3	7.8	67.2	4.0	0.4	3.2	
83	35.0	0.22	35.22	316	16.8	23	8.3	4.4	83.9	1.8	0.3	1.5	
84	35.0	0.63	35.63	116	15.0	27	6.3	у.4	82.8	1.1	0.7	0.5	
85	35.0	1.08	36.08	69	14.9	32	5.2	9.5	83.3	0.8	0.9	0.2	
86	53.9	0.22	54.11	485	11.6	9	52.6	4.9	30.0	3.4	0.5	5.8	
87	53.9	0.63	54.53	176	12.5	14	12.4	13.9	70.0	2.1	0.9	1.3	
88	53.9	1.08	54.98	104	12.4	17	9.1	12.5	75.6	1.7	1.1	0.4	
90	77.8	0.63	78.43	252	7.4	11	23.9	9.0	59.6	2.9	0.2	1.6	
91	77.8	1.08	78.88	149	7.3	12	13.3	9.1	72.7	3.2	0.3	1.2	
20	35.0	0.22	35.22	316	50.5	64	3.9	8.9	85.2	0.8	0.4	0.7	
21	35.0	0.63	35.63	116	49.8	76	1.9	9.2	87.6	0.5	0.5	0.3	
22	35.0	1.08	36.08	69	47.5	79	0.8	9.9	88.9	0.4	0.6	0.2	
23	53.9	0.22	54.11	485	29.8	22	12.9	11.3	72.4	1.3	0.4	1.8	
<b>24</b>	53.9	0.63	54.53	176	29.9	39	5.2	13.0	80.0	0.8	0.7	0.4	
25	53.9	1.08	54.98	104	31.4	41	4.7	15.4	78.1	0.7	0.8	1.5	
26	77.8	0.22	78.02	698	18.2	10	58.0	5.2	28.3	2.9	0	5.5	
27	77.8	0.63	78.43	252	16.6	17	12.3	8.6	74.6	1.9	0.7	1.3	
28	77.8	1.08	78.88	149	15.6	20	11.5	10.9	73.8	2.2	0.8	0.7	
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### Acetylene

Data from Table IV show that at low plasma enthalpy predominantly ethylene is formed along with small concentrations of ethane and higher amounts of methane.

Methane formation increases with plasma enthalpy, and at the highest levels investigated ethane and  $C_{3+}$  hydrocarbons tend to disappear. Increasing hydrogen to carbon ratio favours the formation of saturates, *i.e.* methane and ethane. No pronounced effect of residence time has been found.

			H/C         Plasma enthapy kcal/mole         Conversion C <sub>1</sub> -basis         Selectivity (C <sub>1</sub> -basis) % to           CH4         C <sub>2</sub> H4         C <sub>2</sub> H5         C <sub>4</sub>									
Run No	Run Feed moles/hr No. H C H total		H/C ratio	Plasma enthapy	Conversion C <sub>1</sub> -basis	Selectivity (C <sub>1</sub> -basis) % to						
	H <sub>2</sub>	C <sub>2</sub> H <sub>8</sub>	total		kcal/mole	%	CH4	C <sub>2</sub> H,	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>8</sub>	C <sub>2</sub> H <sub>6</sub>	C,
137	35.0	0.26	35.26	136	18.7	54	37.6	8.7	52.7	0.6	0.5	0
138	35.0	0.7	35.77	48	20.9	46	20.7	10.4	64.7	1.3	0.6	0
139	35.0	1.12	36.12	34	18.8	45	18.2	11.8	68.2	1.3	0.6	0
140	53.9	0.26	54.16	208	14.0	40	56.9	5.7	36.5	0.7	0.3	0
141	53.9	0.77	54.67	73	14.0	32	37.3	12.4	48.0	1.5	0.6	0
142	53.9	1.12	55.02	51	12.6	29	29.4	15.5	56.6	1.6	0.6	0
143	77.7	0.26	77.96	298	8.2	32	74.1	6.5	27.9	0.7	0.1	0
144	77.7	0.77	78.47	104	8.2	27	44.8	8.4	45.3	1.0	0.5	0
145	77.7	1.12	78.82	72	8.1	27	36.7	10.8	50.7	1.3	0.7	0
134	35.0	0.26	35.26	136	35.9	56	38.4	7.6	52.5	0.9	0.4	0
135	35.0	0.77	35.77	48	29.3	50	21.6	11.6	64.4	1.3	0.5	0
136	35.0	1.12	36.12	34	30.0	48	16.6	12.7	68.8	1.4	0.5	0
128	53.9	0.26	54.16	208	16.5	49	55.3	5.4	38.3	0.7	0.3	0
129	53.9	0.77	54.67	73	17.7	37	35.0	9.5	53.6	1.2	0.6	0
130	53.9	1.12	55.02	51	17.5	34	25.4	11.2	61.5	1.3	0.7	0
131	77.7	0.26	77.96	298	12.2	41	66.6	3.6	28.8	0.7	0.3	0
132	77.7	0.77	78.47	104	12.1	35	44.3	6.5	47.7	1.0	0.5	0
133	77.7	1.12	78.82	72	11.8	32	36.0	7.6	54.7	1.2	0.6	0
122	35.0	0.26	35.26	136	39.3	78	39.8	11.1	47.9	0.9	0.3	0
123	35.0	0.77	35.77	48	37.7	63	23.4	14.1	60.8	1.1	0.7	0
124	35.0	1.12	36.12	34	36.9	61	19.2	15.2	63.7	1.2	0.7	0
119	53.9	0.26	54.16	208	29.9	68	51.5	6.9	40.3	0.9	0.4	0
120	53.9	0.77	54.67	73	29.2	54	30.9	10.1	55.9	1.2	0.5	0
121	53.9	1.12	55.02	51	26.1	53	22.4	10.8	56.4	1.2	0.6	0
125	77.7	0.26	77.96	298	19.2	57	65.6	3.8	29.3	0.9	0.5	0
126	77.7	0.77	78.47	104	19.0	47	41.8	7.9	48.5	1.2	0.5	0
127	77.7	1.12	78.82	72	18.9	42	30.7	9.1	55.9	1.3	0.6	0

Table IIEthane experiments

#### Discussion

At extrapolated zero hydrogen-to-carbon ratio *methane* decomposes under all conditions mainly into acetylene and to a lesser amount to ethylene; no ethane and higher hydrocarbons are formed under these conditions. The amount of acetylene is the greater the longer the time of contact. Acetylene formation is clearly the higher the greater the time of contact and the plasma enthalpy.

Run	F	eed, moles	/hr	H/C	Plasma	Conversion		Selecti	vity (C1-b	asis) %	to	
No.	H <sub>2</sub>	C <sub>2</sub> H,	total	ratio	kcal/mole	%	CH,	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>2</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H	C,
74	35.0	0.29	35.29	121	11.8	52	51.2	10.8	34.3	2.6	0.4	0.8
75	35.0	0.78	35.78	46	11.4	42	24.9	6.9	62.4	3.3	1.0	1.4
76	35.0	1.23	36.23	31	11.2	41	17.0	5.3	72.2	3.4	0.8	1.4
77	53.9	0.29	54.19	185	9.7	68	58.6	14.6	22.7	2.9	0.4	0.9
78	53.9	0.78	54.68	71	9.6	41	32.7	11.5	48.0	5.0	0.8	2.0
79	53.9	1.23	55.13	46	9.5	42	22.4	6.7	63.4	5.1	0.6	1.9
80	77.7	0.29	77.99	266	6.8	84	62.3	18.9	15.8	2.4	0.2	0.7
81	77.7	0.78	78.48	102	7.1	41	32.8	14.1	45.4	5.5	0.9	1.3
82	77.7	1.23	78.93	65	6.9	37	28.8	8.9	52.9	7.1	0.7	1.6
62	35.0	0.29	35.29	121	24.1	89	39.8	2.6	56.4	0.5	2.2	
63	35.0	0.78	35.78	46	23.5	76	23.0	3.5	71	. ]		
64	35.0	1.23	36.23	31	23.2	70	16.8	3.4	77	¢1.3	0.8	1
58	53.9	0.29	54.19	185	17.7	94	59.4	4.1	35	0.5	0.3	0.2
57	53.9	0.78	54.68	71	16.1	74	37.3	7.3	521	1.9	0.9	0.5
56	53.9	1.23	55.13	46	18.7	75	24.4	4.8	65.9	2.1	0.9	0.5
59	77.7	0.29	77.99	266	12.8	95	69.5	10.7	18.3	0.8	0.2	0.4
60	77.7	0.78	78.48	102	13.3	74	43.9	9.2	42.8	2.5	0.8	0.9
61	77.7	1.23	78.93	65	13.3	63	33.7	8.5	52.3	0.5	0.6	1.4
68	35.0	0.29	35.29	121	28.9	90	33.6	1.9	63.8	0.1	0.3	0.2
69	35.0	0.78	35.78	46	28.5	90	15.9	1.0	82.4	0.2	0.4	0.2
70	35.0	1.23	36.23	31	29.6	90	12.1	0.7	86.4	0.4	0.4	0.2
65	53.9	0.29	54.19	185	23.9	93	49.8	1.7	47.4	0.4	0.3	0.3
66	53.9	0.78	54.08	71	23.7	87	29.4	1.7	67.5	0.5	0.4	0.5
67	53.9	1.23	55.13	46	22.1	85	18.0	1.5	79.3	0.5	0.4	0.4
71	77.7	0.29	77.99	266	18.3	96	62.9	3.1	32.8	0.4	0.3	0.4
72	77.7	0.78	78.48	102	17.9	86	35.6	3.0	59.7	0.8	0.6	0.4
73	77.7	1.23	78.93	65	17.8	82	27.2	2.6	68.2	0.8	0.6	0.5

Table IIIEthylene experiments

The primary product of *ethane* decomposition at zero H/C ratio is acetylene and a small amount of ethylene. Methane is possibly formed too. Acetylene formation is again favoured at higher contact times and higher plasma enthalpies.

*Ethylene* primarily gives acetylene at zero hydrogen-to-carbon ratio. Ethane, high boiling hydrocarbons and mainly methane appear at higher

				Acetylen	e experime	ents						
Feed, moles/hr			H/C	Plasma	Conversion	Selectivity (C1-basis) % to						
	C,H,	total	ratio	kcal/mol	%	CH,	C.H.	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>3</sub> H	C,	
	0.23	35.23	157	19.3	7	50.7	7.3	37.5	1.3	2.0	0.9	
	0.68	35.68	63	19.4	5	35.0	5.3	53.8	1.2	3.5	0.8	
	1.13	36.13	32	19.1	3	34.9	3.2	53.2	0.9	7.2	0.6	
	0.23	54.13	240	12.7	16	54.1	10.6	31.9	1.1	1.3	0.7	
	0.68	54.58	81	13.3	5	35.4	4.1	55.2	1.1	4.3	0.7	
	1.13	55.03	49	12.3	4	31.5	3.8	56.0	1.0	7.0	0.5	
	0.23	77.93	346	6.4	20	51.7	13.5	32.4	1.3	0.9	0.2	
	0.68	78.38	116	6.8	11	47.3	9.4	40.3	0.9	1.8	0.4	
	1.13	78.87	70	6.6	7	44.4	8.6	42.6	0.4	4.2	0.4	
	0.23	35.23	157	26.1	16	55.3	5.9	33.7	2.1	1.6	0.7	
	0.68	35.68	53	25.8	7	42.7	4.9	43.6	3.0	4.6	0.6	
	1.13	36.13	32	26.2	5	40.4	3.7	49.0	1.5	7.0	0.4	
	0.23	54.13	240	19.4	25	60.0	7.7	27.7	1.6	1.7	0.9	
	0.68	54.58	81	18.9	13	48.0	6.1	39.8	1.3	4.1	0.6	
	1.13	55.03	49	19.5	9	37.2	6.0	47.8	1.6	6.7	0.5	
	0.23	77.93	346	13.9	29	55.1	19.2	21.0	1.7	0.9	1.5	
	0.68	78.38	116	14.2	14	45.8	9.8	38.7	2.0	3.0	2.0	
	1.13	78.87	70	14.1	9	40.6	7.9	43.5	1.8	5.6	0.5	

Table IV

Run No.

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1.13

35.23

35.68

36.13

54.13

54.58

55.03

77.93

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157

53

32

240

81

49

346

116

70

H/C ratios. Again, formation of acetylene is favoured at higher contact times, lower H/C rations, and high plasma enthalpies.

32.9

36.4

29.8

20.4

21.2

20.7

15.7

15.6

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30

13

9

36

19

14

53

27

17

69.4

47.1

44.5

68.7

55.0

49.5

74.3

61.4

53.4

4.5

3.4

2.4

5.6

4.2

3.7

5.9

5.3

4.6

22.9

44.0

47.4

23.2

36.7

41.5

17.2

29.7

37.1

1.3

2.1

0.7

1.2

1.5

1.4

1.2

1.3

1.5

1.3

3.2

4.9

0.9

2.1

3.5

0.8

1.9

3.0

0.6

0.3

0.2

0.4

0.5

0.4

0.7

0.5

0.4

Acetylene is converted to ethylene and possibly methane at zero hydrogen to carbon ratios. Increasing plasma enthalpy but slightly increases acetylene decomposition pattern. High boiling compounds as well as ethane are also formed, especially at low enthalpies.

## Formation of C<sub>3</sub> hydrocarbons

Gas chromatographic analysis showed the presence only of propane, propylene and  $C_4$  hydrocarbons; no higher hydrocarbons could be detected. The formation of propane and  $C_4$  hydrocarbons was very pronounced at low conversions of *methane*; propylene was present always in smaller amounts than the former hydrocarbons. It is interesting to note that no  $C_4$ -hydrocarbons at all could be detected with *ethane* and here also propane was present always at higher concentrations as propylene. *Ethylene* gave considerable amounts of propane at intermediate conversion levels, with  $C_4$ -concentrations being in the same order as propylene. Contrary to these, *acetylene* behaved differently, as propylene was the main heavy component, propane and  $C_4$ -s being present in smaller concentrations.

Comparing results of runs with different hydrocarbons at the same hydrogen-to-carbon ratio, specific plasma enthalpy and flow rate, product compositions differ markedly indicating that the residence time to establish equilibrium within the plasma flame was short compared to reaction rates leading to equilibrium.

The reactivity, i. e. conversion under comparative reaction parameters increased in the following order:

#### acetylene < ethylene < ethane < methane

It is of special interest that acetylene, of the highest thermodynamic stability of all compounds investigated, decomposes to a considerable extent under the test conditions. From this it follows that the final choice of reaction parameters for plasma decomposition of hydrocarbons to yield acetylene must be a compromise, where process conditions have to be balanced to give an optimum acetylene yield.

Further investigations to explain the reactions occurring by means of isotope techniques and mass spectrometry are under way and will be reported later.

## Acknowledgements

The authors wish to thank Miss E. DUDÁS and J. KÁLMÁN, both chemical engineers, for the precise experimental work, and F. GALINA for giving some useful hints with respect to the construction of the electric power source. Thanks are also extended to the Management of the Danube Refinery, Százhalombatta, Hungary, for the generous financing of the research project on plasma chemistry, some results of the work done being published here.

#### Summary

Separate conversions of methane, ethane, ethylene and acetylene were studied in a micro plasma reactor, having a power source of max. 2 kW output. Net plasma power was varied at three levels in the range of 400 to 1800 kcals/hour. Results are discussed also at extrapolated zero hydrogen-to-carbon ratio. At zero H/C ratio methane decomposes mainly into acetylene and to a lesser amount to ethylene. Ethane behaves similarly. Ethylene primarily gives acetylene at zero H/C ratio, while acetylene is converted to ethylene and possibly methane under these conditions. Some  $C_3$  and  $C_4$  hydrocarbons were also detected in the product gases.

The reactivity, *i. e.* conversion of the studied compounds increased in the following order (under comparative reaction parameters)

acetylene 
$$<$$
 ethylene  $<$  ethane  $<$  methane.

It is of special interest that acetylene, of the highest thermodynamic stability of all compounds investigated, decomposes to a considerable extent under the test conditions.

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