

Dec. 9, 1969

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3,483,107

METHOD FOR IMPROVING THE PERFORMANCE OF RADIO FREQUENCY
PLASMA JETS AND THE PRODUCTION OF ACETYLENE

Filed Dec. 5, 1966

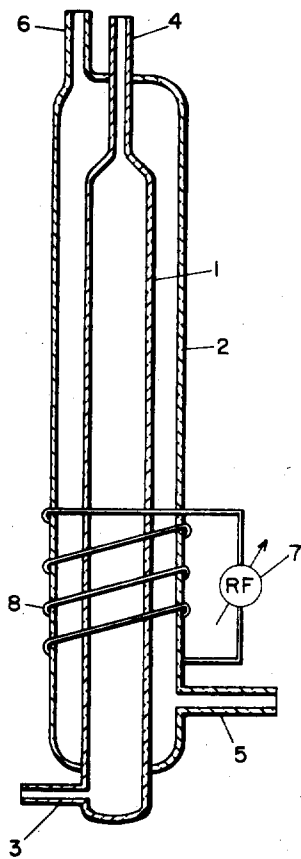


FIG. 1

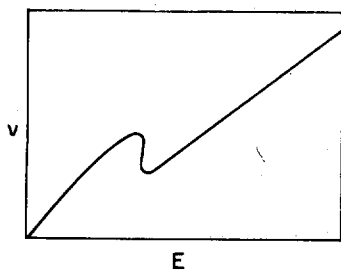


FIG. 4

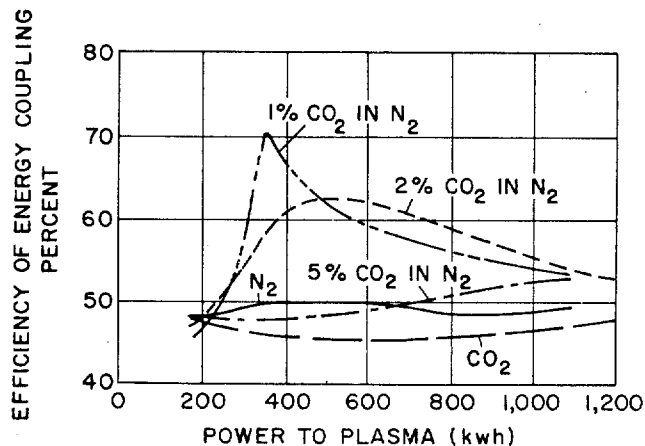


FIG. 2

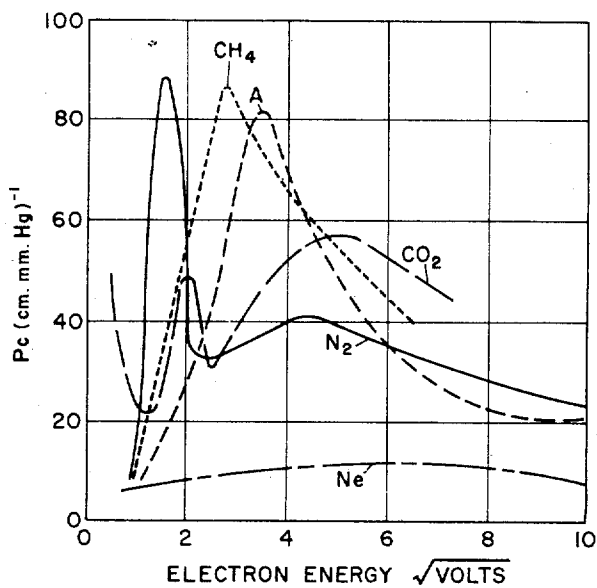


FIG. 3

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METHOD FOR IMPROVING THE PERFORMANCE OF RADIO FREQUENCY PLASMA JETS AND THE PRODUCTION OF ACETYLENE

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Filed Dec. 5, 1966, Ser. No. 599,284

Int. Cl. C07c 3/24; B01j 1/10

U.S. Cl. 204—162

4 Claims

ABSTRACT OF THE DISCLOSURE

The performance of radio frequency plasma jets is improved by flowing a stream of mixed gases having diverse collisional cross sections as a plasma through a tube having low dielectric loss, at least one gas of said stream being present in an amount of not more than about 2 molar percent as a collisional seed gas, inductively coupling the plasma within the tube to a radio frequency source, controlling the frequency of the radio frequency source at from about 10 to about 100 megacycles, and controlling the power level of the radio frequency source to impart low electron energy to the plasma at from about 1 to about 25 electron volts whereby increased energy coupling of the gases within the plasma is effected. The improvement is demonstrated for the conversion of methane into acetylene.

This invention relates to a method for improving the performance of radio frequency (R.F.) plasma jets.

The utilization of R.F. plasma jets for conducting gaseous chemical reactions is perhaps better known than for other considerations such as propulsion, power conversion, radiation source and the like where improved performance is highly desired. Even so, there is much to be desired in the way of improvement in known chemical reactions using the plasma jet where, for example, nitrogen and oxygen are reacted to yield nitric oxide for conversion to nitric acid; nitrogen and hydrogen are reacted to produce hydrazine; nitrogen, hydrogen and oxygen are reacted to produce hydroxylamine; or nitrogen and a hydrocarbon, for example, methane are reacted to produce hydrogen cyanide.

It is a primary object of the present invention to provide a method for improving the performance of a R.F. plasma jet which in addition to chemical reactions, other fields of utilization are benefited to a considerable degree. The attainment of this object will be evident as the specification proceeds with the novel features and combinations being set forth in the appended claims.

According to the present invention, there is provided a method for improving the performance of a radio frequency plasma jet which comprises: flowing a stream of mixed gases having diverse collisional cross sections as a plasma through a tube having low dielectric loss, at least one gas of said stream being present in an amount of not more than about 2 molar percent as a collisional seed gas, inductively coupling the plasma within the tube to a radio frequency source, controlling the frequency of the radio frequency source at from about 10 to about 100 megacycles, and controlling the power level of the radio frequency source to impart low electron energy to the plasma at from about 1 to about 25 electron volts whereby increased energy coupling of the gases within the plasma is effected.

A preferred embodiment of the invention has been chosen for purposes of illustration and description and is shown in the accompanying drawing forming a part of the specification wherein:

FIGURE 1 depicts a suitable apparatus for practicing the invention;

FIGURE 2 is a graph demonstrating the energy coupling efficiency of a binary plasma as obtained in practicing the invention;

FIGURE 3 is a graph demonstrating the probability of collision for different gases including those used in FIGURE 2 to demonstrate the energy coupling efficiency of the present invention; and

FIGURE 4 is a graph showing a typical plot for a negative conductivity plasma.

In the apparatus of FIGURE 1, an inner transparent quartz tube 1 had an outer quartz tube 2 jacketed thereabout. The inner tube 1 was 36 mm. ID and the outer tube was 39 mm. O.D. The inner tube 1 had a gas inlet 3 in the bottom thereof and a gas outlet 4 in the top thereof. The inner tube 1 was of constant diameter throughout about 12 inches of its length whereupon it was necked down to form the gas outlet 4. The outer tube 2 had a water inlet 5 near the bottom thereof and a water outlet 6 in the top thereof. The outer tube 2 was of constant diameter and about 14 inches in length. A radio frequency source 7 was inductively coupled to the apparatus in the lower portion thereof by a coil 8. The coil 8 had a 2 inches ID and a 2 3/4 inches OD, was 3 1/2 inches in length and was wound with 5 1/2 turns of 3/8" OD copper tubing. The R.F. source 7 was capable of being operated at a frequency of from about 10 to about 100 megacycles and at a power level of from 0 to 1500 watts. The apparatus was designed to withstand sub-atmospheric or superatmospheric pressure within the inner tube 1.

An example of the operation of the invention for imparting increased energy coupling of gases is as follows. A binary mixture of CO₂ in N₂ as a plasma was passed through the apparatus of FIGURE 1 by way of gas inlet 3 and gas outlet 4 at different levels of concentration of the CO₂ in the N₂. The apparatus was operated at atmospheric pressure with a gas velocity of 100 ml./sec. and was cooled by cooling water being passed into inlet 5 and from outlet 6. The power level of the R.F. source 7 was varied for each concentration of CO₂ in N₂ as well as for each of these gases alone. The inductance produced an "H" type electrodeless plasma wherein the oscillating R.F. magnetic field induces azimuthal eddy currents in the conductive plasma. The R.F. energy coupled into the plasma was measured by measuring the temperature rise of an opaque fluid (which was circulated through the jacket tube 2). The R.F. input power of the R.F. source 7 was measured with an R.F. wattmeter.

FIGURE 2 shows that the efficiency of energy coupling to the plasma is increased when gas mixtures employing the principle of the invention are used. The individual peaks in the curves result from the shift in the electron energy with R.F. power level. As seen from FIGURE 2, the efficiency can be raised from 50 to 70 percent by simply using binary combinations with the proper conditions, but the binary mixture must contain only a small proportion of the added seed gas. In larger ratios, the seed gas no longer has a controlling effect.

Although it is not intended that the invention shall be limited to any particular theory of operation, it appears that the Ramsauer effect is a controlling factor in respect to practicing the invention. Ramsauer and Kollath (C. Ramsauer and R. Kollath, Am. Physics, 3, p. 536 (1929); R. Kollath, Phy. Zett., 31, p. 985 (1930)) studied the scattering of electron beams at low electron energies (1-25 e.v.) and discovered that the elastic collision cross section exhibited maximum and minimum values in this low energy range. This effect is now called the Ramsauer

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effect and it is the use of this effect in specialized cases with which the present invention is concerned.

FIGURE 3 shows the total cross section for the probability of collision of various gases. These collision cross sections are total cross sections and include both elastic and inelastic collisions, i.e.:

σ total = σ elastic + σ inelastic (ionization, excitation, attachment)

The probability factor is related to the electrons entering and leaving a collision zone by $n = n_0 e^{-p P_c x}$, where:

e = electrons

n_0 = electrons entering the collision zone

n = electrons leaving the collision zone

p = pressure

x = path length in collision zone

P_c = collision probability

From FIGURE 3 it can be seen that molecules like neon have a nearly constant collision cross section while argon has a peak and then trails off as $1/v$. at higher electron energies. Other molecules such as CO_2 and N_2 have a number of minima and maxima in the low electron energy region.

In review, therefore, it would be expected that the collision cross section would increase as the electron energy is decreased. This does occur until the electron energy is in the (1-25 e.v.) range. At this point various resonance effects occur because of the wave-like nature of the electrons. The "electron waves" interact with the potential field of the atom causing diffraction of the electrons.

It will be appreciated that the deBroglie wavelength of an electron is given by:

$$\lambda = h/mv \quad (1)$$

The kinetic energy of an electron moving through a potential γ is:

$$1/2 mv^2 = e\gamma \quad (2)$$

Combining these two equations we have:

$$\lambda = \frac{h}{(2emv)^{1/2}} = \frac{1.23(10^{-10})}{(v)^{1/2}} \text{ meters} \quad (3)$$

When this wavelength is comparable to the effective "radius" of the molecule or atom, the electron is diffracted by the electrical field of the molecule. It can thus be seen that the properties of gaseous plasmas operating with electron energies in the 1-25 e.v. range are strongly controlled by the Ramsauer effect.

Binary gaseous plasma systems are hereinafter analytically defined where electrons are supplying energy to gas molecules A and B. These electrons are receiving power from the electrical field (eEv) and a condition of equilibrium is assumed where the energy gained in the electric field is equal to the energy lost in collision. The following parameters are stipulated:

λ = electron mean free path

C = mean speed of random motion of electron

v = drift velocity of electron in electric field E

W = energy of electron

F_a = fraction of electron energy lost per collision with molecule A

σ_a = collision cross section for molecule A

n_a = number density of molecule A

E = electric field strength

γ = gamma

λ = lambda

σ = sigma

ENERGY BALANCE

Electron gains energy from electric field by:

$$eEx \quad (4)$$

Transit time for x :

$$x/V \quad (5)$$

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Time between collisions (ΔT):

$$\lambda/c \quad (6)$$

Number of collisions in distance x :

$$5 \quad xc/\lambda v \quad (7)$$

Energy lost by electron in distance x :

$$Fw = xc/\lambda v \quad (8)$$

10 For equilibrium in distance x :

$$eEx = Fwxc/\lambda v \quad (9)$$

MOMENTUM BALANCE

During the time interval between collisions, ΔT , the electron will travel a distance given by:

$$x' = v\Delta T \quad (10)$$

$$X' = 1/2 a (\Delta T)^2 = 1/2 \left(\frac{eE}{m} \right) (\Delta T)^2 \quad (11)$$

20 Thus:

$$1/2 \frac{eE}{m} \frac{\lambda}{c} = v \quad (12)$$

and

$$2vc = \frac{eE\lambda}{m} \quad (13)$$

Combining Equations 9 and 13 and assuming

$$30 \quad W = 1/2 mc^2$$

the following relationship exists:

$$v^2 = 1/4 F_c^2 \quad (14)$$

In considering a gas mixture of A and B, the fraction of the electron energy lost per collision is given by:

$$F = \frac{n_a \sigma_a F_a + n_b \sigma_b F_b}{n_a \sigma_a + n_b \sigma_b} \quad (15)$$

Formulae 14 and 15 permit the designing of a gaseous plasma with properties amenable to high performance of energy coupling from the source to the gas.

In considering a binary gas mixture:

$$45 \quad v^2 = 0.25 \frac{(n_a \sigma_a F_a + n_b \sigma_b F_b)}{n_a \sigma_a + n_b \sigma_b} c^2 \quad (16)$$

The importance of drift velocity control is evident from energy coupling considerations in plasma devices.

In considering Equation 16, various cases arise where the velocity factor is controlled by some minor constituent or by the fact that a collisional parameter is rapidly changing.

Consider the following conditions:

Case 1

$$n_a \sigma_a \sim n_b \sigma_b$$

where:

$$n_a \sim n_b \text{ or } n_a > n_b$$

$$\sigma_a \sim \sigma_b \quad a < \sigma_b$$

then:

$$65 \quad v^2 = 0.25 \frac{(F_a + F_b)}{2} c^2$$

Thus, a low concentration of component B provided its collision cross section is much greater than component A has a strong effect on the electron properties within the plasma. Yet the properties of the plasma are those of component A. Typical examples would be low concentrations 1-5 m/o of argon in helium or neon.

Case 2

$$n_a \sigma_a > n_b \sigma_b$$

$$F_a > F_b$$

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In this case gas A is obviously the controlling parameter.

Case 3

$$n_a \sigma_a > n_b \sigma_b$$

$$F_a < F_b$$

where:

$$n_a \sigma_a F_a \sim n_b \sigma_b F_b$$

In this case, both A and B control the plasma properties.

Case 4

$$n_a \sigma_a > n_b \sigma_b$$

$$F_a < F_b$$

where:

$$n_a \sigma_a F_a \ll n_b \sigma_b F_b$$

In this case:

$$v^2 = 0.25 \frac{(n_b \sigma_b F_b)}{n_a \sigma_a} c^2$$

and if σ_b/σ_a can decrease faster than C^2 increases with increasing E, an important situation develops. In this case, or region, v will decrease as E increases. Thus is designated a "negative conductivity" plasma. A typical v vs. E plot would look as depicted in FIGURE 4.

This condition thus places a stabilizing influence on the plasma properties as E increases keeping the drift velocity within a region where maximum energy transfer is possible, i.e., where collisional parameters are maximized.

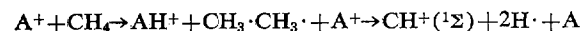
Example.—Experiments were conducted to show how the energy yield of a chemical reaction can be improved by using a seed gas in conjunction with a primary chemical reactant. For the purposes of this illustration, the conversion of methane into acetylene using argon as the seed gas to complete the binary mixture was selected.

In order to avoid the quenching problem associated with operating a radio-frequency plasma jet at high pressure and high enthalpy, the system was operated at low pressure, <1 torr, where gas temperatures were held to values only slightly higher than room temperature. The electron energy could then be varied to high values 20–30 ev. through the range where binary effects would occur in the gas mixture.

Because the system involves a chemical reaction, there are two effects which will occur which may be mutually masking.

First, at low concentrations of the seed gas, one could expect the energy coupling into the binary mixture to increase. FIGURE 3 shows the collision cross sections for both argon and methane and it is readily seen that only in the range of electron energies of 7–12 ev. will this effect occur.

The second effect involves an ion-molecule reaction between argon and methane molecule fragments. There is evidence (2) which indicates that the CH radical formed in the 2π ground state from methane is the only one which reacts appreciably to form acetylene. Argon ions can undergo in the present of methane ion-molecule reactions which can lead to the formation of precursors of the $CH(2\pi)$ radical. Thus:



Both of these reactions are extremely rapid, particularly the second because in this reaction the energy defect is practically zero, i.e.

$$I_p CH_3 = 15.58 \text{ ev.}$$

$$I_p A = 15.755 \text{ ev.}$$

The resultant electron recombination with the CH^+ would lead to the formation of the following excited states $CH(2\Delta)$, $CH(2\Sigma^-)$. These would decay rapidly to the ground state $CH(2\pi)$ yielding radiation bands at 3900 Å. and 4315 Å., respectively. Spectroscopic evidence in our laboratory shows strong emission at 3900 Å. with mixtures of argon and methane. With the addition of argon at higher concentrations, I would then expect a re-

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duction in the ethane concentration of the off-gas and an increase in the acetylene concentration. Σ , π and Δ as used above refer to orbital angular momentum of the electrons.

A summary of key experiments is shown in Tables 1 and 2.

TABLE 1
G-value* of Acetylene Production from Methane

Experiment	Reaction (nominal concentration)	G-value
1.....	CH ₄	0.025
2.....	2 m/o A in CH ₄	0.049
3.....	5 m/o A in CH ₄	0.026
4.....	10 m/o A in CH ₄	0.054
5.....	50 m/o A in CH ₄	0.078

*G-value=molecules C₂H₂/100 ev. deposited in discharge.

The increase in the G-value at low concentrations of the argon seed gas is attributed to the collisional effects. The increase in the G-value at higher concentrations results from the increased occurrence of ion-molecule reactions.

The off-gas analysis also supports this conclusion:

TABLE 2

Experiment	Reaction (nominal concentration)	Off gas-(carbon based)		
		C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
1.....	CH ₄	24.6	7.2	50.6
2.....	2 m/o A in CH ₄	24.6	5.5	55.3
5.....	50 m/o A in CH ₄	32.7	11.8	39.2

These experiments show that the collisional effects at low seed concentrations can improve the product yield; however, the ion-molecule effects at higher seed concentrations produce a more dramatic effect of increasing the product yield.

The apparatus used to conduct the experiments was similar in principle to that of FIGURE 1 with the exception that it included a liquid nitrogen trap for collecting the condensable gases.

From the foregoing it is evident that there are numerous factors which will influence conditions for the most satisfactory operation of the invention; the actual limits of which cannot be established except by a detailed consideration of each set of gases to be utilized in the plasma to effect efficient energy coupling and the utility for which the plasma is desired. Generally, in multi-gas or binary gas systems, the gases will include hydrogen, air, carbon monoxide, nitrogen, hydrocarbon gases and mixtures thereof as the primary gas and will include argon, carbon dioxide, helium, neon, and mixtures thereof as the seed gas and wherein the latter is present in an amount of not more than about 2 molar percent of the primary gas. Although the data demonstrating the present invention were obtained under atmospheric conditions and a gas velocity of 100 cc/sec., subatmospheric and superatmospheric pressures may be utilized in the range from about 1 torr to about 2 atmospheres with gas velocities up to sonic velocity. The R.F. plasma as utilized in accordance with the present invention utilizes frequencies in the range of from about 10 to about 100 megacycles where the energy coupling method is inductive and is used to transfer the primary R.F. energy into the plasma and where the power input level imparts low electron energy to the plasma at from about 1 to about 25 electron volts. The plasma in this case is normally a gas which is about 1 to 10 percent ionized.

The advantages of the present invention are multifold. The erosion and contamination problems associated with other plasma jets, such as the arc-jet are alleviated by this method. This is why the R.F. plasma jet has attracted much attention in the crystal growing industry. Also, the initiation of the R.F. discharge is comparatively simple and the average enthalpy level of the R.F. generated plasma can be much higher than other plasma generating devices since the R.F. discharge can be made

much more uniform and be distributed over a larger gas volume. Thus, applications requiring a dense, high temperature, stable, uniform, uncontaminated plasma can be satisfied by the R.F. plasma discharge.

A number of applications where increased energy coupling efficiency leads to a useful application of the R.F. plasma jet in accordance with the present invention are as follows:

In propulsion, the high enthalpy plasma jet has been cited as a low thrust to weight propulsor with a specific impulse in the 800-2,000 sec. range. An arc-jet is presently envisioned as the propulsor. The R.F. propulsor suffers in two respects; low conversion efficiency for such gases as hydrogen and helium ~50% and a high specific weight for the R.F. power source (generator). If the energy coupling efficiency can be raised 20-30% to approach that of the arc-jet device, the R.F. high enthalpy propulsor could become competitive with the arc-jet on certain electrical propulsion missions which normally require high energy R.F. equipment for mission purposes such as communication satellites, deep space probes, electronic counter measures satellites, etc. On these missions, the penalty of an R.F. power source of high specific weight is partially compensated by mission requirements. Thus, for the R.F. propulsor a low molecular weight gas "seeded" with a gas forming a strongly absorbing binary couple as previously discussed is desired.

In plasma chemistry, most plasma chemistry reactors for potential industrial chemicals employ an arc-jet source of high temperature gas. As in other cases, the R.F. plasma jet suffers from low efficiency in energy coupling. In many cases, a feed gas is passed through the plasma reactor and heated to high temperature. The problem of efficiently coupling energy into this feed gas often arises. The gas must serve a dual purpose. It is serving as a reactant as well as an energy coupling medium. In the second case, it must possess the requisite electrical properties or it may not function as an efficient coupler of energy. A binary gas system where the absorbing gas is an inert would greatly improve the performance of such a system. It would be of low enough concentration to increase the efficiency thereby improving the cost picture. Many plasma jet processes use hydrogen as a feed gas. A binary system such as argon in hydrogen would improve the economics of these systems.

In power productions, numerous methods of obtaining non-equilibrium ionization in a simple high temperature gas have been sought for use in an MHD power generator. This method implies that the electron concentrations are well above those which are accounted for by thermal ionization. Presently, easily ionizable metal vapors are used such as cesium to seed the gas stream such as helium to increase the electrical conductivity at relatively low temperatures. For a closed cycle system, this entails the use of expensive separators to recycle the seed material. In the presence of an electric field, magnetic fields have been used to increase the effective collision cross section of electrons. This increase can also be affected by the use of binary gas systems as has previously been shown. The low concentration of seed gas does not affect the overall hydrodynamic properties of the gas stream.

And in radiation sources, electrically heated gases (flash

tubes) and shock heated gases (explosively driven) can serve as light sources for optically pumping laser devices. The brightness temperature of these devices can be extended beyond that common to inert, low specific heat, atomic gases such as xenon by the addition of small quantities of gases having strong effects on the collisional properties of the binary gas mixture. The higher brightness temperature of the optically dense gas mixture results from the added radiating species present in the discharge. The bulk thermal properties of the gas remain the same as the original constituent.

It will be seen, therefore, that this invention may be carried out by the use of various modifications and changes without departing from its spirit and scope, with only such limitations placed thereon as are imposed by the appended claims.

What I claim and desire to protect by Letters Patent is:

1. A method for improving the performance of a radio frequency plasma jet which comprises:

(a) flowing a stream of primary gas and secondary seed gas having diverse collisional properties as a plasma through a tube having low dielectric loss, the molar ratio of the primary gas to the secondary seed gas being from about 50 to 1 to about 200 to 1, said primary gas being a gas of the group consisting of hydrogen, air, carbon monoxide, nitrogen, hydrocarbon gases, and mixtures thereof and said secondary seed gas being a seed gas of the group consisting of argon, carbon dioxide, helium, neon, and mixtures thereof,

(b) inductively coupling the plasma within the tube to a radio frequency source,

(c) controlling the frequency of the radio frequency source at from about 10 to about 100 megacycles, and

(d) controlling the power level of the radio frequency source to impart low electron energy to the plasma at from about 1 to about 25 electron volts whereby increased energy coupling of the reactive gases within the plasma is effected.

2. The method according to claim 1 wherein at least two of the gases utilized are reactive gases.

3. The method according to claim 1 wherein the seed gas is present in an amount of not more than about 2 molar percent of the primary gas.

4. The method according to claim 1 wherein the seed gas is argon and the primary gas is methane as the hydrocarbon gas for the production of acetylene.

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BENJAMIN R. PADGETT, Primary Examiner

U.S. Cl. X.R.

250-43; 313-231; 315-111