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Factors Influencing the Decomposition of CO_2 in AC Fan-Type Plasma Reactors: Frequency, Waveform, and Concentration Effects

Stephanie L. Brock,* Tomoko Shimojo,*,† Manuel Marquez,*,‡ Carolina Marun,§ Steven L. Suib,*,§,¶,[1] Hiroshige Matsumoto,‖ and Yuji Hayashi**

*U-60, Department of Chemistry, §Department of Chemical Engineering, and ¶Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-4060; †Department of Applied Chemistry, Waseda University, Tokyo, Japan; ‡Department of Electrical Engineering and Applied Physics, Yale University, New Haven, Connecticut 06511; ‖Department of Chemistry, Nagasaki University, Bunkyomachi 1-14, Nagasaki, 852 Japan; and **Research and Development Laboratories, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya, 456 Japan

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The decomposition of CO_2 in fan-type ac glow discharge reactors coated with platinum or rhodium was studied as a function of concentration of CO_2 in the feed, frequency, and waveform shape. The progress of the reaction was monitored with an ion-quadrupole mass spectrometer coupled with a partial pressure analyzer. CO was the main carbonaceous product with selectivities >80%. Mixtures of 2.5, 10, and 20% CO_2 in He were studied and the conversion is observed to increase with decreasing CO_2 concentration, although the power consumed by the reactor remains relatively constant. The reaction efficiency for the reaction (proportional to yield) is observed to increase with increasing CO_2 concentration. The frequency has little effect on the conversion of CO_2 in the plasma, but the plasma power consumption is observed to decrease as the frequency is increased at constant applied voltage, resulting in an increase in reaction efficiency with increasing frequency. The conversion of CO_2 increases with increasing input voltage in the range 411–2050 V root mean square (rms), then levels off up to 10.91 kV rms. The plasma power shows the same trend as conversion, whereas the efficiency and excitation temperature of the plasma are observed to decrease up to 2050 V rms and then level off. The effects of sine, square, and triangular waveforms were examined and found to yield similar conversions, plasma powers, and efficiencies. The order for conversion and power is square > sine > triangular and the order for efficiency is triangular > sine ≈ square. CO_2 conversion is maximized for a square waveform and low concentrations of CO_2 at input voltages near 2 kV rms. Conversion is independent of the ac frequency. Conversely, maximization of reaction efficiency occurs at low input voltages (<2 kV rms) and high concentrations of CO_2 with a triangular waveform at frequencies in the kiloHertz range. Optimization of conditions has resulted in an efficiency of 11.4% for CO_2 dissociation to CO and O_2.

INTRODUCTION

Emission of carbon dioxide from combustion of fossil fuels has become a global concern due to projected climatic changes associated with an enhanced greenhouse effect (1–3). As such, research has focused on techniques for remediation, including trapping in geological formations (4) and new markets for large-scale use of CO_2 as a supercritical fluid (5) and as a source of energy (6). The key to CO_2 as an energy source may involve its conversion to CO, which could be used in synthesis gas or as a reactant to form high-energy products. Thermal methods for CO_2 activation have been successful in both of these endeavors; however, to date, they are not feasible from an energy efficiency standpoint (7–8). The use of plasmas may provide a way of activating CO_2 without the large energy cost associated with thermal methods (9, 10).

The decomposition of CO_2 has been explored under a variety of plasma conditions including arc discharge plasmas (11–13), which can reach temperatures of several thousand Kelvins, and room temperature corona discharges (14, 15). The effect of added gases such as hydrogen, nitrogen, and argon on the conversion and product distribution has also been explored (6, 16). Theoretical exploration of the impact of various parameters, such as vibrational excitation (17), quenching rates (18), and collision processes (19) have resulted in many improvements in the conversion and selectivity of CO_2 plasma reactions. Novel methods for CO_2 remediation, such as its decomposition to form O_2, which could be subsequently recycled, improving engine combustion (20), and formation of carbonates as part of a flue gas cleaning system for NO_x, SO_x, and CO_2 (21), have also been studied and show some promise. Use of an ac ferroelectric packed bed reactor has decomposed up to 108 g of CO_2 per kiloWatt hour of pure, applied energy (10); however, the energy efficiency of this and other reactions is still not adequate for practical consideration of large-scale CO_2 remediation. Current concern about the greenhouse effect and our environment demand that we redouble our efforts in this area.

Recently, we have begun an investigation of the dissociation of CO_2 in atmospheric pressure plasmas generated in

[1] To whom correspondence should be addressed.

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fan-type glow discharge reactors coated with various metal catalysts. Such reactors are being employed in our group for the decomposition of various atmospheric pollutants, as well as the formation of novel materials (22, 23). The effects of the metal catalyst, flow rate, input voltage, and diluent gas with respect to conversion and energy efficiency of CO_2 dissociation have recently been established in this system (24, 25). Additionally, spectroscopic studies have provided insight into the mechanism of CO_2 activation and the role of the metal catalyst in the reaction. In this investigation, we have turned our attention to other parameters important to the plasmochemical dissociation of CO_2: concentration of CO_2, frequency of the ac signal, and shape of the ac signal (sine, square, or triangular waveform). The conversion and reaction efficiency of the dissociation of CO_2, as well as the excitation temperature of the plasma, will be discussed with respect to these three parameters and our previous study on the plasma decomposition of CO_2.

EXPERIMENTAL

Plasma reactor. The CO_2 dissociation reactions were run in Plasma and Catalysis Integrated Technologies (PACT) fan-type reactors (26, 27) consisting of an inner rotor with a diameter of 5.59 cm and 10 evenly spaced fan blades protruding 0.34 cm from the fan. The outer electrode, the stator, has an inner diameter of 6.33 cm, producing an electrode gap of 0.3 mm. The width of the fan is 1.66 cm and the plasma volume is approximately 0.25 cm^3. The rotor and stator have been coated with Pt or Rh using electroless plating. Rotation was effected by the insertion of a fan motor, controlled by a variac to a speed of 3600 revolutions per minute (rpm), into the rotor.

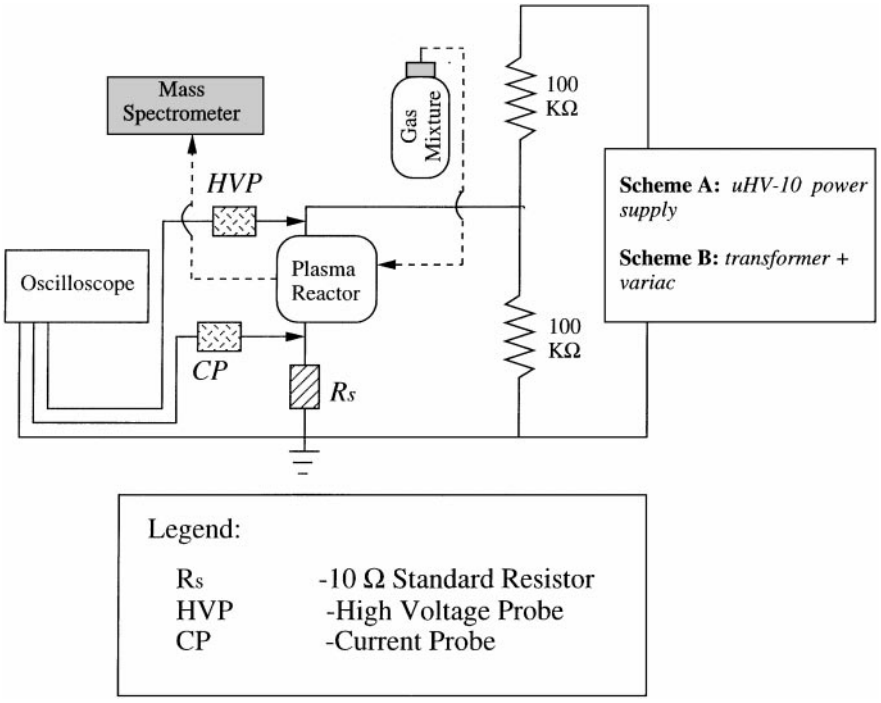
Experimental setup. Three different setups are employed, depending on the power supply used. Schemata are presented in Fig. 1. Setup A employs a Japan-Inter uHV-10 ac high-voltage generator operating at 8.1 kHz with a nonconventional waveform (Fig. 2A) and setup B uses a transformer and variac high-voltage supply with a constant frequency of 60 Hz and a sinusoidal waveform (Fig. 2B). The voltage and current conditions of the plasma were monitored using a Tektronix 6015A high-voltage probe and a Yokogawa digital oscilloscope DL1520, and the current was monitored by measuring the voltage across a 10-Ω resistor placed in series. An ac voltage of 400–900 V rms was placed across the gap between the rotor (ground) and stator to produce the plasma. Setup C uses a Trek model 10 : 10 amplifier and a Wavetek function generator with variable frequency, waveform, and high voltage controls. The Trek has built-in high-voltage and current probes which are connected to the Yokogawa oscilloscope. The frequency is varied between 60 and 12050 Hz and the voltage between 0.84 and 10.9 kV rms. Data were taken using sine, square, and triangular waveforms (Figs. 2B, 2C, and 2D). The plasmas were run at atmospheric pressure using 1.25, 2.5, 10, and 20% of CO_2 in He with gas flow rates of 30–100 cc/min. The gas temperature in the reactor is approximately 50°C, measured by inserting a temperature probe into the reactor immediately after shutting off the plasma. The plasma power was calculated by integrating the product of the current and voltage waveforms.

Product analysis and spectroscopic studies. Product analysis was carried out with an MKS-UTI PPT quadrupole residual gas analyzer mass spectrometer (MS) with a Faraday cup detector and a variable high pressure sampling manifold. Carbon dioxide conversions were measured from the change in signal of the $m/e = 44$ peak, which is proportional to the partial pressure of CO_2. Carbon monoxide and oxygen were quantified by monitoring the $m/e = 28$ and $m/e = 32$ signals, respectively. Spectroscopic studies were carried out using a 270 M Spex instrument with a CCD detector. A fiber-optic cable was used to collect the light and direct it to the monochromator. A wavelength range of 200–900 nm was used for the studies and the helium emission lines are accurate to ± 0.1 nm.

RESULTS

The dissociation of CO_2 in fan-type plasma reactors coated with metal catalysts was studied as a function of CO_2 concentration, frequency of the ac high-voltage signal, input voltage, and waveform shape. The CO_2, CO, and O_2 concentrations in the product stream were analyzed with a mass spectrometer with partial pressure analyzer (MS-PPA). CO_2 conversion, plasma power, and reaction efficiency and plasma excitation temperature data are presented. Conversions were calculated by the change in the $m/e = 44$ signal and selectivities to CO by the ratio of $m/e = 28$ to $m/e = 44$. Plasma power was calculated by integrating the product of the voltage and current waveforms. The reaction efficiency, in percent, was calculated using the following equation: $100 \times E_c/E_p$, where E_c is the calculated free energy for the dissociation of CO_2 to CO and O_2 (257 kJ/mol) and E_p is the energy consumed in the plasma. Selectivities to CO were determined to be >80%, justifying the efficiency calculation. The reaction efficiency is proportional to the yield divided by the power. The excitation temperatures (T_{exc}) were calculated for a pure helium plasma as a function of frequency and input voltage. The values are computed from the intensity of the helium emission lines according to the equation $\ln(I\lambda/gA_{kj}) = E_k/k_B T_{exc}$, where I is the integrated intensity of the helium emission, λ is the wavelength, g is the statistical weight of the level, A_{kj} is the transition probability, E_k is the excitation energy of the upper level, and k_B is the Boltzmann constant (28).

Concentration effects. In order to probe the effects of the concentration of CO_2 in He on conversion and efficiency



Scheme C:

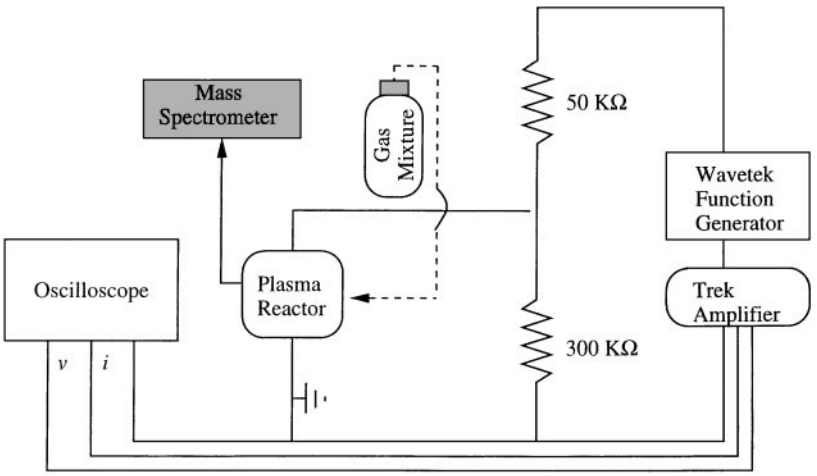


FIG. 1. Schemata of the experimental setup for generation of the plasma and monitoring of the voltage and current characteristics: (A) Japan-Inter uHV-10 power supply, 8.1 kHz; (B) variac controlled transformer, 60 Hz; (C) Trek 10 : 10 amplifier and Wavetek function generator with variable frequency, voltage, and waveform.

of the dissociation reaction, data were taken for three different CO_2 concentrations: 2.5, 10, and 20%. The data were obtained with the Japan-Inter uHV-10 power supply with a fixed frequency of 8.1 kHz (Fig. 1, Scheme A) using a Pt-coated reactor. The data as a function of concentration for an input voltage of 711 V rms and a flow rate of 60 cc/min are presented in Table 1 and plotted in Fig. 5. As the concentration of CO_2 is increased, there is a nearly linear decrease in conversion; however, the plasma power changes very little. The efficiency is therefore proportional to the yield and is observed to increase with increasing concentration. As illustrated in Table 1 and Figs. 3 and 4, the 10 and 20% CO_2 mixtures show the same trend for conversion and efficiency as the 2.5% CO_2 mixture. As the input voltage increases, the conversion of CO_2 increases and the efficiency decreases. For the 10 and 20% CO_2 mixtures it is not possible to ignite or sustain a plasma at 411 V rms input as it is for the 2.5% CO_2 in He mixtures. Thus, among the parameters described here, the highest conversion is obtained for a 2.5% CO_2 in He mixture at an input voltage of 906 V rms (16.7%),

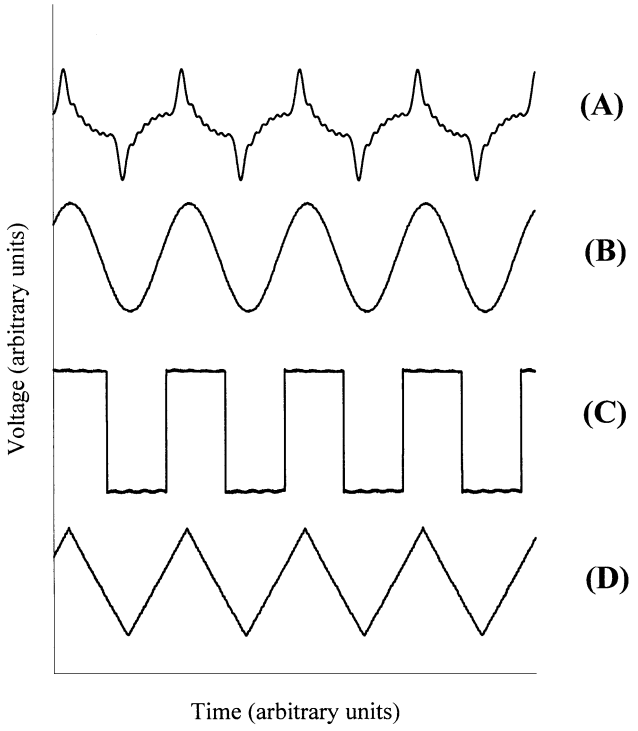


FIG. 2. Illustration of the signal outputs from the various power supplies. (A) Nontypical, uHV-10; (B) sine, Wavetek and transformer; (C) square, Wavetek; (D) triangular, Wavetek.

TABLE 1

Percentage Conversion of CO_2, Plasma Power, and Percentage Reaction Efficiency of CO_2 Dissociation as a Function of Input Voltage (V_{in}) and Concentration of CO_2 in He for a Pt Fan-Type Plasma Reactor

	CO_2 concentration in He		
V_{in} (V, rms)	2.5% CO_2	10% CO_2	20% CO_2
711			
Conversion (%)	14.1	9.71	6.70
Plasma power (W)	1.79	1.70	1.82
Efficiency (%)	2.08	6.00	7.73
906			
Conversion (%)	16.7	11.22	8.29
Plasma power (W)	2.58	2.64	2.71
Efficiency (%)	1.71	4.47	6.43

Note. The standard deviations for the conversion, plasma power, and efficiency are ≤5% of the value.

whereas the highest efficiency is achieved with a 20% CO_2 in He mixture at 711 V rms input voltage (7.73%).

Frequency and waveform effects. Initial attempts to probe the effect of frequency involved the comparison of the Japan-Inter uHV-10 power supply with a fixed frequency of 8.1 kHz (Fig. 1, Scheme A) to a transformer controlled by a variac with a fixed frequency of 60 Hz (Fig. 1, Scheme B). The variac was used to adjust the input voltage from the transformer to be similar to that obtained with the

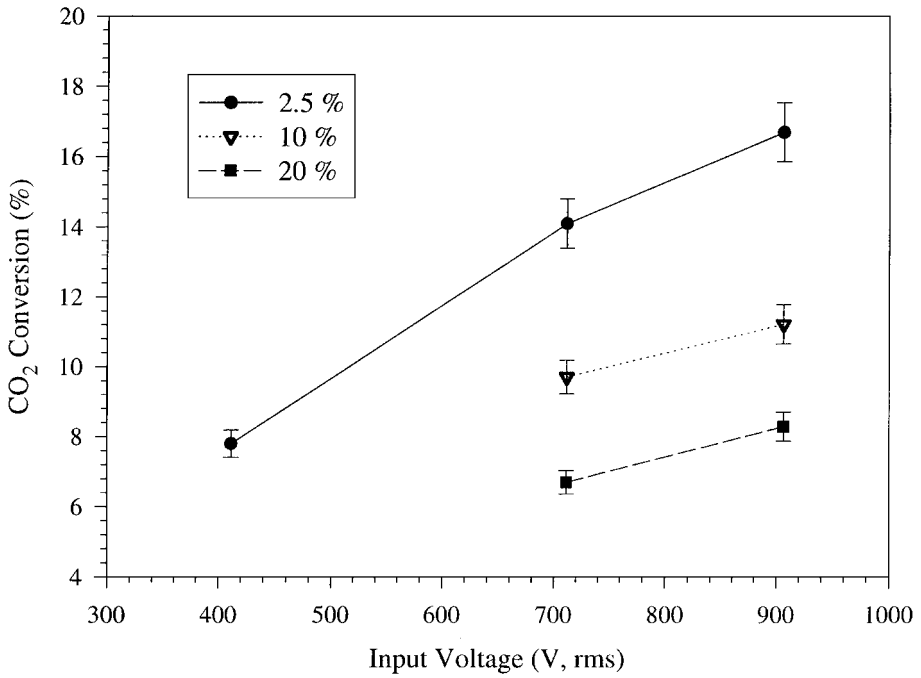


FIG. 3. Percentage conversion of CO_2 in 2.5, 10, and 20% CO_2 in He gas mixtures as a function of input voltage for the Pt-coated reactor. For the 10 and 20% CO_2 mixtures, no plasma is produced at 411 V rms input voltage.

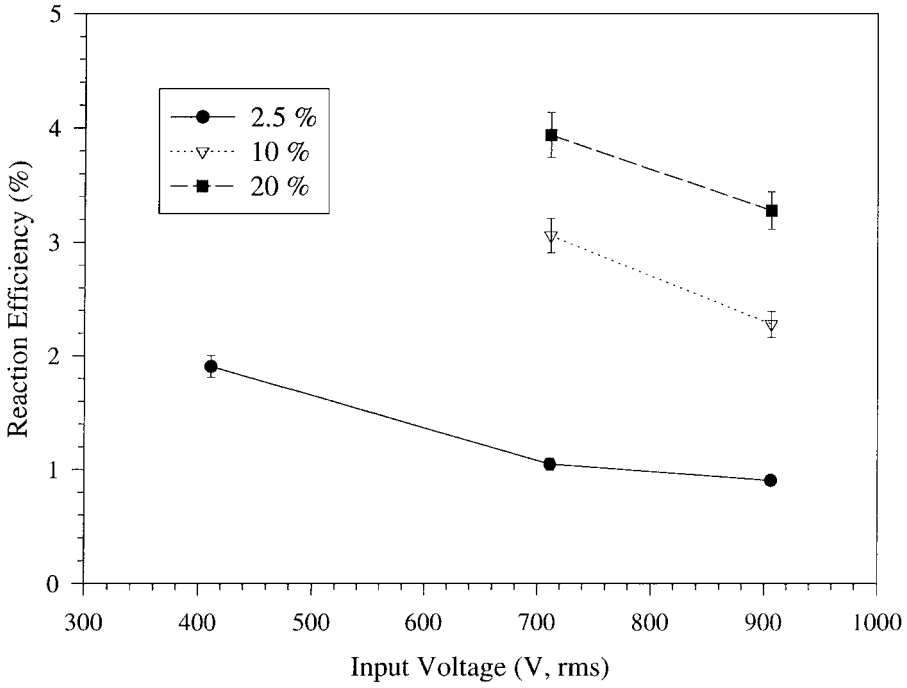


FIG. 4. Percentage reaction efficiency for the dissociation of CO_2 to CO and O_2 for mixtures of 2.5, 10, and 20% CO_2 in He as a function of input voltage for the Pt-coated reactor. For the 10 and 20% CO_2 mixtures, no plasma is produced at 411 V rms input voltage.

uHV-10. A mixture of 2.5% CO_2 in He at a flow rate of 30 cc/min was employed in the reaction with the Rh-coated fan-type plasma reactor. The results of the study are presented in Table 2. For a similar rms input voltage, the conversions obtained with the transformer at 60 Hz were lower than those obtained with the uHV-10 (25.2% vs 30.5%) and the power consumed by the reactor was greater (3.33 W vs 2.78 W). If the peak to peak voltages of the uHV-10 and

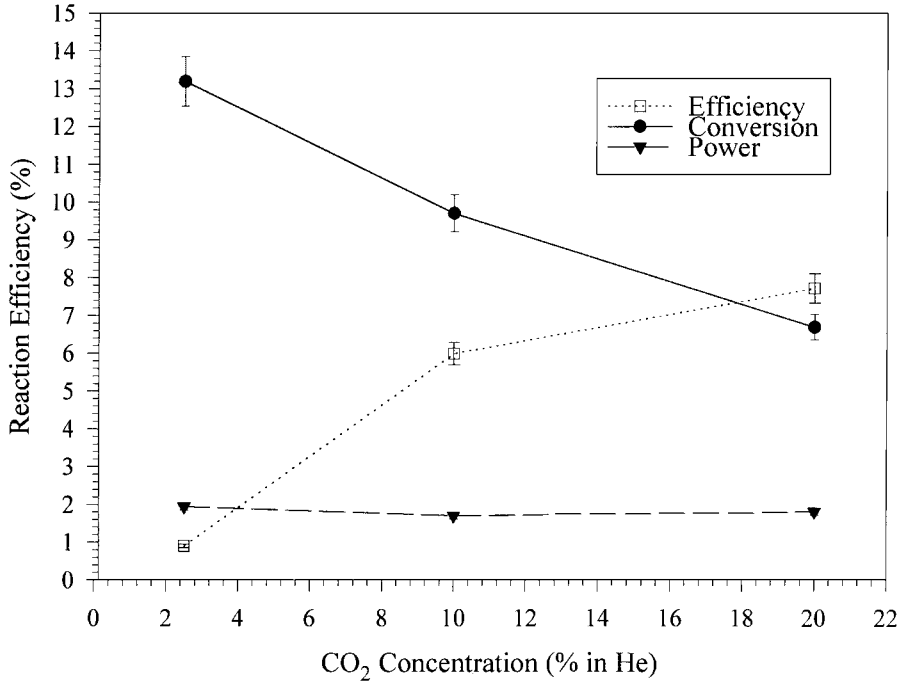


FIG. 5. CO_2 conversion (%), reaction efficiency (%), and plasma power (W) as a function of the concentration of CO_2 in the CO_2/He mixtures for a Pt-coated reactor. The flow rate is 60 cc/min and the input voltage is 711 V rms.

TABLE 2

Percentage Conversion of CO_2, Plasma Power, and Percentage Reaction Efficiency for the Dissociation of CO_2 to CO and O_2 as a Function of Power Supply

Power supply	Waveform	V_{in} (kV, rms)	$V_{p\text{-}p}$ (kV)	Conversion (%)	Power (W)	Efficiency (%)
uHV-10, 8.1 kHz	Nonconventional	0.867	2.18	30.5	2.78	0.74
Transformer, 60 Hz	Sine	0.878	1.24	25.2	3.33	0.51
Transformer, 60 Hz	Sine	1.520	2.18	36.4	7.21	0.39

Note. The peak to peak voltage ($V_{p\text{-}p}$ and root-mean-square voltage (V_{rms}) were varied independently for the transformer to match the values obtained with the uHV-10 generator. Rh-coated reactor, 2.5% CO_2 in He, flow rate = 30 cc/min. The standard deviations for the conversion, plasma power, and efficiency are $\leq$5% of the value.

transformer are instead set to similar values, the transformer yields a higher conversion (36.4%) and higher power consumption (7.21 W) than the uHV-10. Thus, the efficiencies of the reactions performed with the transformer are considerably less than those obtained with the uHV-10 generator. This cannot be unambiguously attributed to the frequency difference between the two power supplies. The fact that the rms and peak to peak input voltages are different when produced by the different power supplies is a function of the difference in waveform shape. The uHV-10 generates a nonconventional waveform illustrated in Fig. 2a, whereas the transformer generates a sine wave (Fig. 2b).

In order to separate out the effects of waveform and frequency, a Wavetek function generator with variable frequency, waveform, and input voltage controls was used along with a Trek amplifier as the power supply for the reaction. A 1.25% CO_2 in He mixture at a flow rate of 60 cc/ min and a Pt coated reactor was used for the study. An input voltage of 2.05 kV rms was maintained and a sine waveform was used as the frequency was varied between 60 and 12050 Hz. The conversion, power, and efficiency data are presented in Table 3 and Fig. 7. As the frequency is increased, the conversion stays approximately the same but the plasma power changes dramatically. There is only a small change over the decade between 60 and 600 Hz, but once in the kHz range the power decreases sharply with increasing frequency. The efficiency is therefore linearly and inversely correlated to the power and thus increases as the frequency is increased. The excitation temperature of a pure helium plasma parallels the conversion data, showing no variation with changing frequency. An excitation temperature of 1670 ± 50 K is obtained at an input voltage of 2.2 kV rms.

The input voltage range attainable with the Trek generator is larger than that obtained with the uHV-10, extending from 0.844 to 10.91 kV rms for a square waveform, relative to 0.411 to 0.906 kV rms for the nonconventional waveform employed with the uHV-10. Thus, the Trek generator permits a study of the effect of input voltage on conversion in a greater range than any we have studied to date. Data were obtained for a 1.25% CO_2 in He mixture at a flow rate of 60 cc/min, a fixed frequency of 600 Hz, a square waveform, and a Pt-coated reactor. The data are presented in Table 4 and Fig. 6. There is an initial increase in conversion between 0.844 kV and 2.05 kV rms input voltage, after which the

TABLE 3

Percentage Conversion of CO_2, Plasma Power, and Reaction Efficiency (%) for the Dissociation of CO_2 to CO and O_2 as a Function of Frequency

Frequency (Hz)	Conversion (%)	Power (W)	Efficiency (%)
61	22.4	10.39	0.28
602	21.9	11.23	0.26
8197	22.8	4.45	0.67
12050	23.3	1.72	1.79

Note. Data are taken with the Trek amplifier and Wavetek function generator using an input voltage of 2.05 rms kV, a sine waveform, and a gas mixture of 1.25% CO_2 in He at a flow rate of 60 cc/min (Pt-coated reactor). The standard deviations for the conversion, plasma power, and efficiency are $\leq$5% of the value.

TABLE 4

Percentage Conversion of CO_2, Plasma Power, and Reaction Efficiency (%) for the Dissociation of CO_2 to CO and O_2 as a Function of Input Voltage

V_{in} (kV, rms)	Conversion (%)	Power (W)	Efficiency (%)
0.844	13.2	2.70	0.65
2.05	24.5	13.13	0.25
2.83	25.2	13.72	0.24
10.91	26.7	14.24	0.25

Note. Data are taken with the Trek amplifier and Wavetek function generator using a frequency of 600 Hz, a square waveform, and a gas mixture of 1.25% CO_2 in He at a flow rate of 60 cc/min (Pt-coated reactor). The standard deviations for the conversion, plasma power, and efficiency are $\leq$5% of the value.

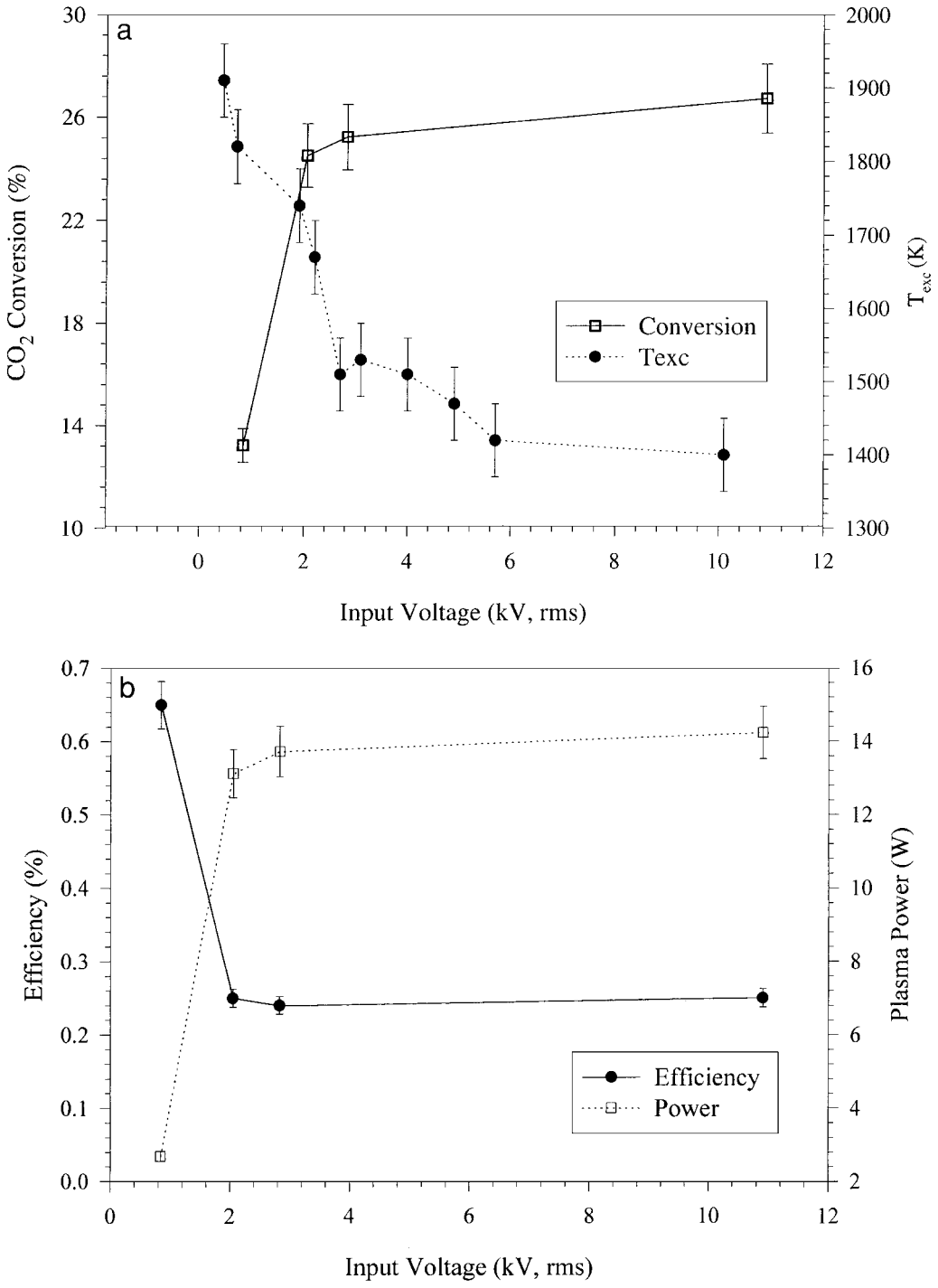


FIG. 6. Input voltage dependence of (a) CO_2 conversion (%) and excitation temperature (T_{exc}, K) of a pure helium plasma and (b) plasma power (W) and reaction efficiency (%) for dissociation of CO_2 to CO and O_2. Plasma parameters: 1.25% CO_2 in He mixture, flow rate = 60 cc/min, frequency = 600 Hz, square waveform, Pt-coated reactor.

conversion is nearly flat all the way up to 10.91 kV rms. The power shows the same trend. The percentage efficiency and the plasma excitation temperature for pure helium show the opposite trend: the efficiency and excitation temperature are greatest at the lowest input voltage used and then decrease up to 2–3 kV rms and become flat above this voltage.

The effect of the waveform on the plasma was explored for sine, square, and triangular wave shapes (Figs. 2B, 2C, and 2D). A 1.25% CO_2 in He mixture, a flow rate of

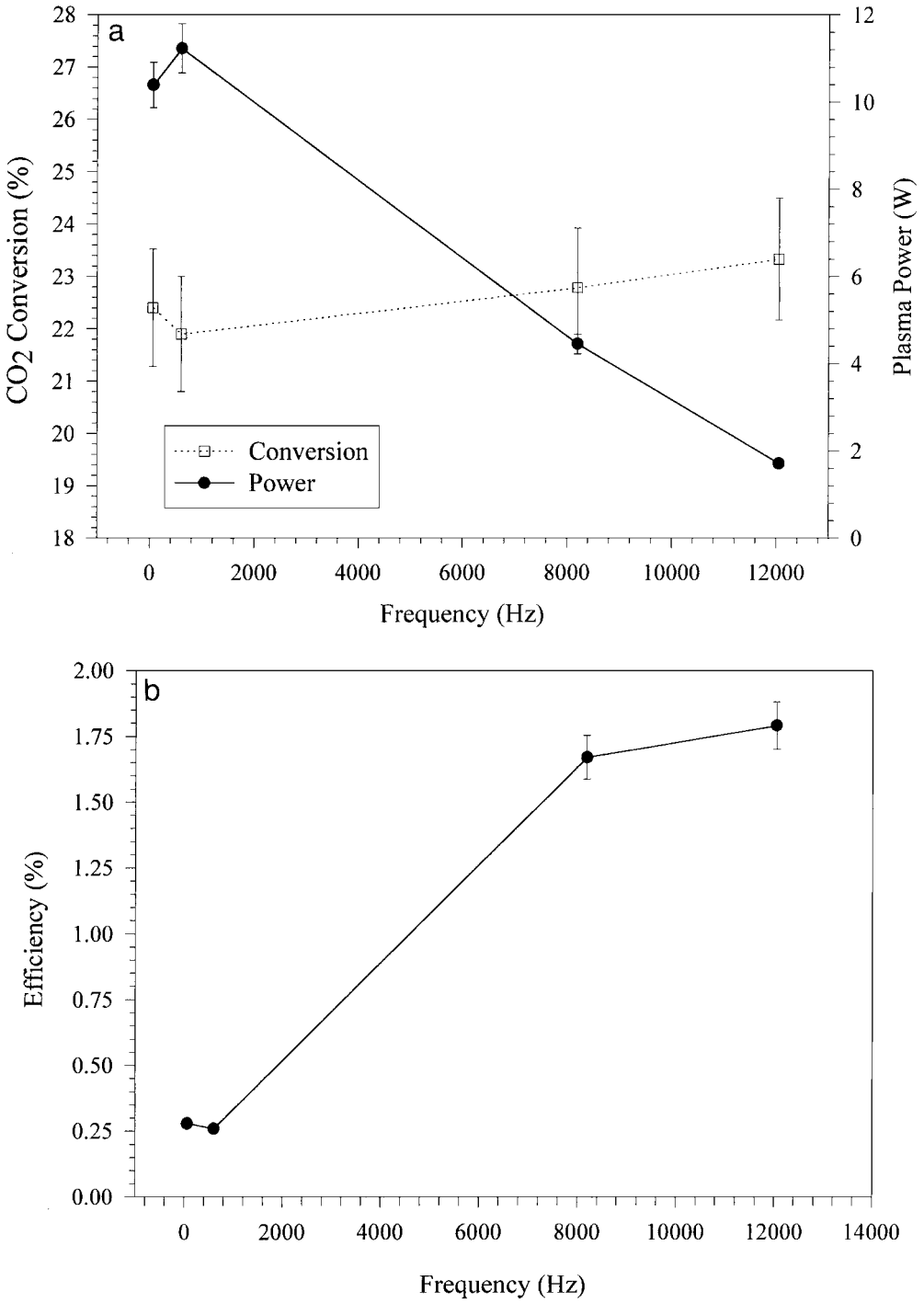


FIG. 7. Frequency dependence of (a) CO_2 conversion (%, left axis) and plasma power (W, right axis) and (b) percentage reaction efficiency for the dissociation of CO_2 to CO and O_2. Plasma parameters: 1.25% CO_2 in He mixture, flow rate = 60 cc/min, input voltage = 2.05 kV rms, sine waveform, Pt-coated reactor.

60 cc/min and a fixed frequency of 600 Hz were used as constant plasma parameters and the conversion, power, and efficiency data are presented in Table 5. Because the rms voltage is dependent upon the shape of the waveform, whereas the peak to peak voltage is not, data were obtained for both square and triangular waveforms at two different settings. In one, the rms voltage (V_{in}) was matched to that of the sine waveform (2 kV), and in the other, the peak to peak voltage ($V_{p\text{-}p}$) was matched (6 kV, shaded data in Table 5). In all cases, the conversion, power, and

TABLE 5

Percentage Conversion of CO_2, Plasma Power, and Reaction Efficiency (%) for the Dissociation of CO_2 to CO and O_2 as a Function of Waveform

Waveform	V_{in} (kV, p-p)	V_{in} (kV, rms)	Conversion (%)	Power (W)	Efficiency (%)
Sine	5.92	2.07	21.9	11.23	0.26
Square	6.04	2.83	25.2	13.72	0.24
Square	4.36	2.05	24.5	13.13	0.25
Triangular	6.00	1.73	22.9	9.85	0.31
Triangular	7.20	2.05	23.6	10.34	0.30

Note. Data are taken with the Trek amplifier and Wavetek function generator at a frequency of 600 Hz for a gas mixture of 1.25% CO_2 in He at a flow rate of 60 cc/min (Pt coated reactor). The peak to peak voltage ($V_{p\text{-}p}$) and root-mean-square voltage (V_{rms}) are varied independently for the square and triangular waveforms to match the values obtained with the sine waveform. The standard deviations for the conversion, plasma power, and efficiency are $\leq$5% of the value.

efficiency data were very similar for the three waveforms. The orders of conversion and plasma power as a function of waveform are square > sine > triangular, whereas the efficiency varies as triangular > sine $\approx$ square.

DISCUSSION

Plasma decomposition reactions depend on a large number of variables. The optimization of these variables is necessary to maximize the efficiency and the conversion of the reaction. We have recently reported (24, 25) the effects of metal catalyst, flow rate, diluent gas, and input voltage on the dissociation of CO_2 in ac plasmas and the results can be summarized as follows. The identity of the metal catalyst is found to have a significant influence on the conversion and efficiency of the reaction. For the five catalyst metals studied, a reactivity order of Rh > Pt $\approx$ Cu > Pd > Au is obtained. Such a metal effect is also reflected in the He emission spectra, and quantum-chemical *ab initio* calculations are under way to try and understand this effect. Conversion and efficiency have opposing trends when correlated to flow rate and input voltage. While a larger percentage of the CO_2 passing through the reactor can be dissociated at lower flow rates, increased flow rate results in a larger yield of dissociated CO_2 over time, thus the efficiency increases. With respect to input voltage, the power is less effectively transferred to the CO_2 dissociation reaction at higher input voltages, resulting in a decrease in efficiency despite the increase in CO_2 conversion. Finally, the identity of the diluent gas has been found to have a pronounced effect on conversion, supporting spectroscopic evidence for energy and charge transfer between diluent gas exited state species and CO_2 as an important pathway to CO_2 dissociation. The relative order for both efficiency and conversion is He > Ar > N_2, consistent with the relative rates for bimolecular energy transfer to CO_2.

Conversions of up to 30.5% have been obtained with gas mixtures of 2.5% CO_2 in He, but the yield and efficiency of dissociated CO_2 is low due to the low concentration of carbon dioxide in the mixture. The use of 10 and 20% CO_2 results in decreased conversions relative to the 2.5% mixture, however, the yields are actually higher for these mixtures and the plasma power does not change much with changing concentration. Thus, the efficiencies of the reaction are observed to increase with increasing CO_2 concentration, from 2.08% for a 2.5% CO_2 mixture up to a maximum efficiency of 6.00 and 7.73% for 10 and 20% CO_2, respectively, at 711 V rms for a Pt reactor. As for the 2.5% CO_2 mixture, conversion increases with increasing input voltage, but efficiency decreases. Unlike the 2.5% CO_2 mixture, no plasma is present at an input voltage of 411 V rms for the 10 and 20% CO_2 in He mixtures. The addition of carbon dioxide increases the resistance of the electric gaseous layer between the electrodes, thus greater input voltages are required to sustain a plasma at high CO_2 concentrations (29).

Frequency is also an important factor in plasmochemical reactions. Depending on the lifetime of the reacting species, various pathways can be turned on or off by adjusting the driving frequency for the plasma. Additionally, the energy distribution among ions and electrons is different at high frequencies, with a smaller proportion allotted to ions which are unable to respond to the quickly oscillating field due to their high mass (relative to electrons) (30). Thus, frequency control may be important to optimize conversions, selectivities, or power administration within the plasma. In this case, variation of the frequency over more than three decades from 60–12050 Hz at a constant applied voltage resulted in no change in conversion or selectivity to CO (generally >90%). However, a large change in power is observed and thus the efficiency of the reaction has a strong dependence on the driving frequency. As frequency is increased, the plasma power is decreased and thus the efficiency increases from 0.26 to 0.28% at 60–600 Hz to 1.79% at 12050 Hz for a 1.25% CO_2 in He mixture at 60 cc/min and an input voltage of 2.05 kV (Pt-coated reactor). Previous studies, including spectroscopic studies performed by

our group (24, 25), have suggested that a dominant pathway for the dissociation of CO_2 involves charge and energy transfer from $He_n^+ (n = 1–3)$ species present in the plasma to form vibrationally excited CO_2^+ which readily dissociates to CO and O upon electron impact (14, 18). The slowest step in this sequence is the energy and charge transfer from He_n^+ which proceeds with a bimolecular rate constant of 16×10^{-10} cm^3/s (31). For frequencies in the range 60–12000 Hz, similar kinetics are readily accessible. It is likely that heat dissipation pathways, such as the acceleration of ions (32), are in effect at low frequencies, in addition to CO_2 dissociative pathways (30, 33). Thus, increasing frequency up to the point where the ions are fixed in the oscillating field (approximately 1 MHz) results in a decrease in the power consumption of the reactor.

The fact that the processes that occur within the plasma which are responsible for the conversion of CO_2 are the same at all the frequencies measured is borne out in the excitation temperature data. The excitation temperature of a pure helium plasma is essentially a measure of the distribution of excited energy states of helium present in the plasma. Because helium plays an important role in the activation of carbon dioxide (*vide infra*), T_{exc} is an important indicator of the ability of plasmas to decompose carbon dioxide. In previous studies, we were able to correlate T_{exc} with conversion for different catalytic metal coatings on the reactor (24, 25). Higher excitation temperatures correlate with lower CO_2 conversions. Conversion and excitation temperature are once again correlated as a function of frequency. Both remain nearly constant over the frequency range studied, 60–12050 Hz.

Input voltages in the range 0.411–0.906 have been studied using the uHV-10 generator (Fig. 1, Scheme A) and conversions increase with increasing input voltages, whereas efficiencies decrease. Use of the Wavetek generator and Trek amplifier permit the investigation of input voltages in a different range: 0.84–10.9 kV rms. Over the range 0.84 to 2.05 kV rms, the conversion and power increase and the efficiency and excitation temperature decrease. However, above 2 kV, conversion, power, efficiency, and excitation temperature change very little, suggesting that the voltage and current which can be sustained by the plasma is maximized for an input voltage of 2 kV (corresponding to a power of >13 W). In all cases we have studied, greater efficiencies are obtained at the minimum input voltage at which a plasma will form.

The shape of the waveform may be expected to alter conversions or selectivities by activating excited states all at once (as in the square wave) or gradually (sine or triangular waveform). However, after the breakdown voltage has been attained and once the plasma is in the normal glow region, the voltage levels off and the main effect of the shape is to control the percentage of time a plasma is present in the reactor. The order is square > sine > triangular with the square wave achieving the breakdown voltage faster than the sine and triangular forms, resulting in a larger relative percentage of time per cycle in which a plasma is present. The effect is a small one with respect to conversion, power, and efficiency. The conversion and power consumed by the reactor both increase in the order square > sine > triangular, but the increase in conversion does not quite match the increased power draw. Thus, the efficiency order is triangular > sine $\approx$ square.

Efficiency is an important measure of practicality for any plasma reaction. This and previous studies of CO_2 dissociation have made clear the effects of various plasmochemical parameters on the efficiency of the reaction. CO_2 concentration, frequency, flow rate, diluent gas, catalyst metal, and input voltage all have a large effect on yields and/or conversions, and the waveform shape has a lesser effect. Optimization of the plasma efficiency within the parameters established through our research should be attained for a 20% CO_2 in He gas mixture, at a frequency of 12050 Hz, a flow rate of 120 cc/min, for as low an input voltage as is accessible (850 V, due to power supply limitation), using a Rh- or Pt-coated reactor (Pt in this case) and a triangular waveform. We have performed studies under these conditions and have obtained an efficiency of 11.4% for the dissociation of CO_2 to CO and O_2 or 70 g CO_2 decomposed per kiloWatt hour of consumed energy, corresponding to a conversion of 5.2% at a power of 1.92 W (consumed). This represents a nearly threefold increase in efficiency from our previous study (24). It is expected that the efficiency can be further increased by better matching of the power supply to the reactor, a further increase in frequency to the MHz range, and an increase in flow rate.

CONCLUSIONS

Plasma decomposition of CO_2 may prove to be an effective and energy efficient technique for CO_2 remediation if the parameters governing the plasmochemical reactions can be optimized. Altering the frequency over the range from Hertz to kiloHertz, while having no effect on conversions, has a pronounced effect on the energy demands of the plasma and thus the energy efficiency of the reaction. Concentration of CO_2 in the feed has little effect on the energy demands of the plasma, but the yield of dissociated CO_2 is greatly affected. It appears that there is a maximum operating input voltage for the system around 2 kV rms, above which there is little change in conversion, power, or efficiency. Finally, the shape of the waveform, although it does not have a dramatic effect, does produce some small changes. Thus, from this and previous studies, maximization of conversion will occur for low concentrations of CO_2 in the feed, at input voltages near 2 kV rms, at low flow rates, independent of frequency. Conversely, the most energy efficient reactions will be obtained for high concentrations of

CO_2 in the feed at low input voltages, high flow rates, with an ac driving frequency in the kiloHertz range. The waveform can also have a small impact on the plasmochemical reactions and a square waveform is found to yield the highest conversions, whereas the triangular waveform produces the highest efficiencies. With respect to catalytic metal, Rh or Pt have been found to yield the highest conversions and efficiencies. To date, we have achieved a maximum efficiency of 11.4% in the fan-type plasma reactor. More studies are underway to further improve the efficiency of plasma CO_2 decomposition.

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