

h	= layer thickness, m
h_1, h_2	= values of h for $Q < Q_m$, m
h_m	= maximum value of h , m
h_j	= discrete values of h , m
L	= length scale in y -direction, m
N	= number of discrete points, dimensionless
p	= fluid pressure, $\text{N}\cdot\text{m}^{-2}$
P	= jet pressure, $\text{N}\cdot\text{m}^{-2}$
P_1	= scaled maximum pressure gradient, dimensionless
Q	= volume flux per unit span, $\text{m}^2\cdot\text{s}^{-1}$
Q_m	= maximum value of Q , $\text{m}^2\cdot\text{s}^{-1}$
t	= time, s
T	= tangential stress in jet, $\text{N}\cdot\text{m}^{-2}$
u	= horizontal fluid velocity, $\text{m}\cdot\text{s}^{-1}$
v	= vertical fluid velocity, $\text{m}\cdot\text{s}^{-1}$
V	= upward speed of sheet, $\text{m}\cdot\text{s}^{-1}$
x	= horizontal coordinate, m
y	= vertical coordinates, m

Greek Letters

ϵ	= measure of surface slope h/L , dimensionless
μ	= fluid viscosity, $\text{N}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$
ν	= μ/ρ
ρ	= fluid density, $\text{kg}\cdot\text{m}^{-3}$
σ	= surface tension coefficient, $\text{N}\cdot\text{m}^{-1}$
τ_{\perp}	= normal stress, $\text{N}\cdot\text{m}^{-2}$
τ_{\parallel}	= tangential stress, $\text{N}\cdot\text{m}^{-2}$
τ	= $\sigma\mu^{1/2}V^{1/2}\rho^{-3/2}g^{-3/2}L^{-3}$, dimensionless

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Plasma Decomposition of Carbon Dioxide

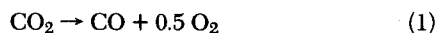
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The energy efficiency of plasmachemical processes seems to be the most important factor which limits their practical application. Most of plasmachemical reactions under investigation are carried out far from optimum conditions, as their mechanism is often not known. Hence there is the necessity of intensive research into the energy efficiency of plasmachemical reactors and into modelling studies.

The objective of the present work was to model some aspects of the plasma decomposition of carbon dioxide based upon the experimental measurements of fundamental process parameters.

Because of the very high dissociation energy for carbon monoxide molecule, CO_2 decomposition at plasma temperatures occurs primarily according to simple equation



Nishimura et al. (1974) observed that even under extreme conditions (reaction temperature as high as 7,500 K) decomposition of CO did not exceed 35%. The simplicity of main reaction, as a model for endothermic homophase processes, is not the only reason for the numerous studies on plasma CO_2 decomposition. There are also some interesting possible uses of the reaction products, mainly as energy sources. Carbon monoxide can be used as an effective

reducing agent in metallurgy, an alternative reagent in catalytic processes of organic chemistry and, in the water conversion reaction as a hydrogen source. The results of studies on plasma CO_2 conversion can be useful in formulating solution for high-temperature combustion problems and in species lifetime predictions for high-power lasers. Finally, the problems of rational CO_2 utilization begins to be important for environmental protection reasons (Wigley et al., 1980).

Butylkin et al. (1979) applied numerical techniques to solution of quenching and kinetics problems in high-temperature CO_2 decomposition process and to determine energy consumptions for oxygen production at different quenching rates. Carbon dioxide decomposition has been studied both in nonequilibrium (Brown and Bell, 1974; Legasov et al., 1977) and equilibrium plasmas. Fractional conversions as high as 70% have been obtained in r.f. argon plasma at temperatures exceeding 6,000 K under atmospheric pressure (Nishimura and Takenouchi, 1976). In contradiction to their previous work (Nishimura et al., 1974), the authors did not confirm the decomposition of the produced carbon monoxide. It was stressed, however, that equilibrium was not reached. Blanchet et al. (1969) reported that only 5% conversion was achieved in a d.c. argon plasma jet. Szymański and Huczko (1978) examined the influence of process parameters on the reaction. The total conversion of CO_2 as high as 60% was attained in an argon plasma. Extensive studies on the reaction run in helium plasma have been carried out by Charette and Parent (1973). The authors

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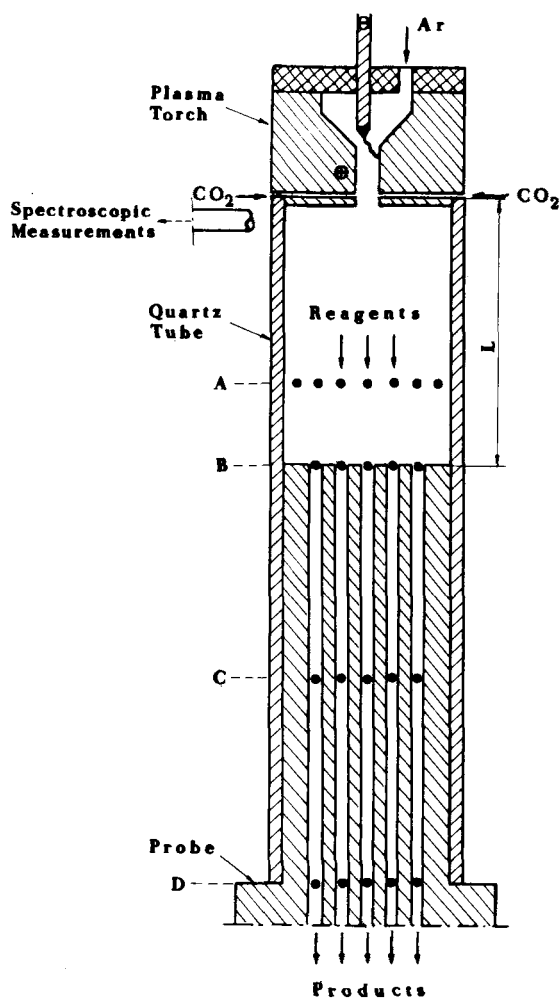


Figure 1. Schematic drawing of experimental apparatus.

studied the process kinetics in its preliminary step, although the conversion was as low as 12% probably due to low quenching rate of products in a plasma calorimetric probe.

The aim of present work was to extend those studies for the argon plasma in the lower temperature range. This region is more favorable both for economic reasons and the possible application of the classical Arrhenius kinetics.

EXPERIMENTAL

The plasma reactor, presented diagrammatically in Figure 1 consisted of a d.c. plasma torch (Szymański et al., 1979) and of a 44 mm ID quartz tube. The arc discharge power at a pressure of close to 1 atm was established at 5 kW. The constant molar flow of plasma gas (Ar) was 2.0×10^{-2} mol/s. Using techniques different from those that had been previously applied by Charette and Parent (1973), carbon dioxide, at various molar flow rates, was introduced into the hottest plasma zone through six orifices (0.05 cm ID) located in a nozzle (0.6 cm ID). The products were withdrawn from the reactor through 0.3 cm ID channels of a water-cooled sampling multichannel probe located at different longitudinal position L in order to measure spatial distribution of both temperature and fractional conversion. Gas samples were analyzed by gas chromatography. Carbon monoxide and oxygen were determined to be the primary reaction products. The presence of ozone which had been previously postulated in modelling nonequilibrium r.f. frequency discharge in $\text{CO}_2\text{--CO--O}_2$ (Brown and Bell, 1974) was qualitatively confirmed. The temperature T_m at different zones A, B, C, D of reactor (Figure 1) was measured by means of platinum/platinum-10% rhodium thermocouple taking into account the gas flow rate correction. The distance between measuring zones was 2 cm for A-B and 9 cm for both B-C and C-D sections. The experimental data collected in each run included: volt-ampere characteristics, cooling water and gases inlet and outlet temperatures and flow rates, and composition of the reaction products. Calorimetric measurements in the system were performed in order to predict the average temperature and velocity of gases. The bulk mean mass temperature T_b of reaction mixture was then calculated from the energy balance.

RESULTS AND DISCUSSION

A thermodynamic study was made for high-temperature CO_2 decomposition. Starting from the equilibrium constant for main

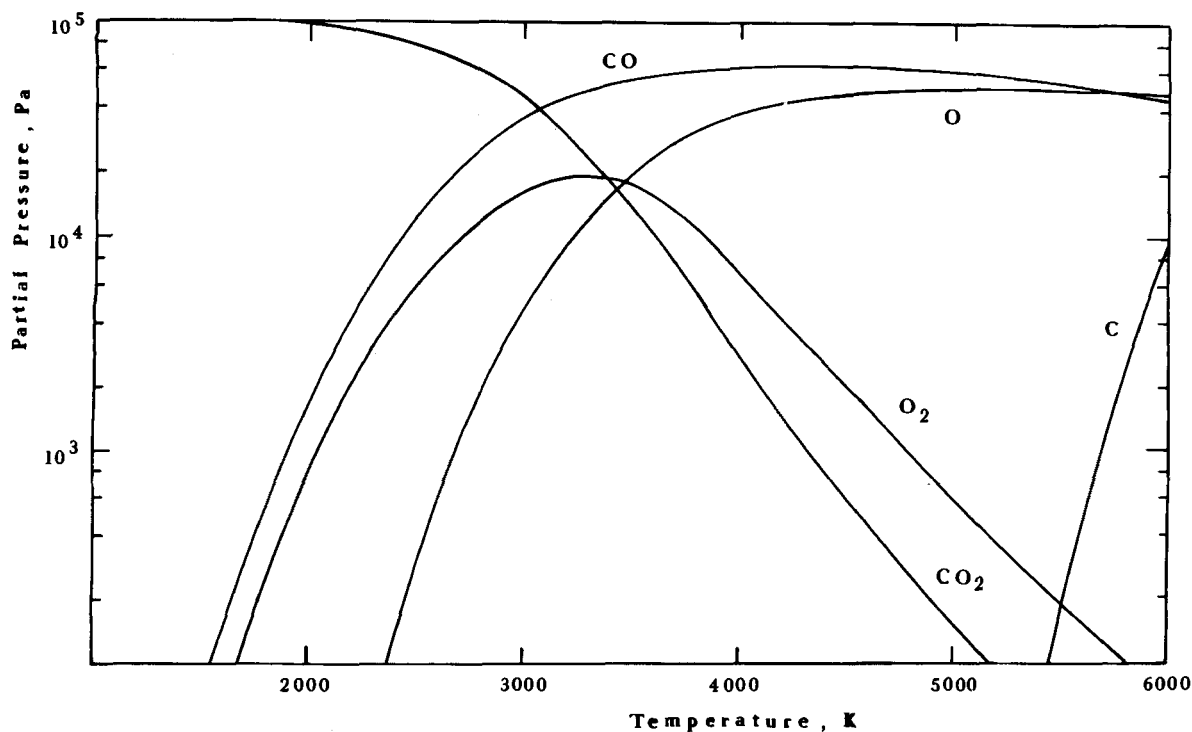


Figure 2. Equilibrium composition of the C-O system. C:O = 1:2.

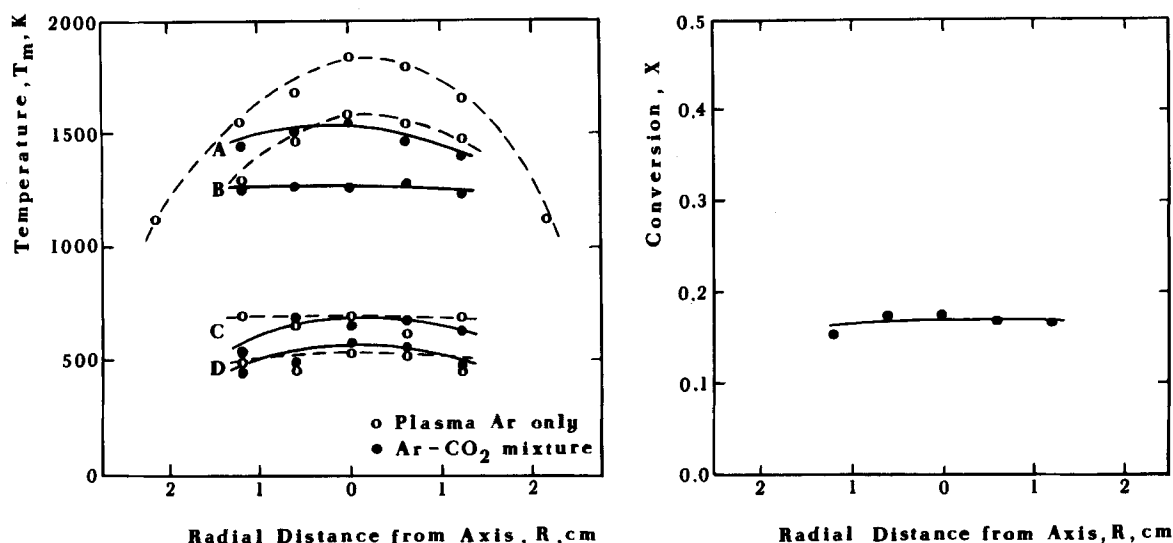


Figure 3. Radial temperature and conversion distributions. Operating conditions: $m_{\text{CO}_2} = 3.7 \times 10^{-3}$ mol/s; $L = 15$ cm.

reactions in the C—O system, the equilibrium composition as a function of temperature was calculated numerically. The results for the assumed ratio C:O = 1:2 at atmospheric pressure, Figure 2, show that over a wide range of temperature, which is characteristic for low-temperature plasma, carbon dioxide effectively dissociates and the predominant products are CO and O_2 .

The radial profiles of temperature and conversion in the system under various carbon dioxide molar flow rates m_{CO_2} and probe longitudinal position have been measured. An example of the experimental results is shown in Figure 3. The calculated mean mass temperature T_b in this case reached 3,700 K. As can be seen, gradients in the radial direction of fractional conversion as well as of temperature for different zones A, B, C and D are relatively small. It is more pronounced for the Ar— CO_2 mixture because of greater stream turbulence and homogeneity caused by addition of cold gas to the Ar plasma stream. Furthermore, the reaction mixture enters the quartz tube through a nozzle of smaller diameter and a recirculation phenomena may take place, as is confirmed by the value of dimensionless Craya-Curtet number for the experimental system (Johnson et al., 1968). Hence the observed low radial gradients of measured parameters and the possibility of averaging them over the cross section.

Measured and calculated values both of averaged temperatures (as an example, for B and C zones) and of fractional conversion d

for variable m_{CO_2} and L parameters are shown in Figure 4. As can be expected, an increase in substrate flow implies that both temperature and conversion decrease for a given L value. An increase in the length of the reaction zone tends to lower the temperature and fractional conversion. The plot of conversion vs. longitudinal distance indicates that for longer reaction times one can expect the reverse reaction to begin. The results of measurements seem to confirm and extend the studies of Charette and Parent (1973) for a longer reaction zone. The authors predicted the existence of a plateau in the \bar{X} vs. L plot, defining the maximum of CO_2 decomposition for a given thermal conditions of the system. It is possible to make a statement now, that a delay in quenching of the reaction products implies the possibility of CO reoxidation.

Temperature measurements made possible an estimate of the quenching rate W in the separate sections of reactor:

$$W = (T_I - T_{II})/t_{I-II} \quad (2)$$

For a given reactor parameters in the system Eq. 2 can be written in the form

$$W = 5.05(T_I - T_{II})^2 [m_{\text{Ar}} + m_{\text{CO}_2}(1 + 0.5\bar{X})]/L_{I-II} \ln(T_I/T_{II}) \quad (3)$$

for quenching in the quartz tube, and

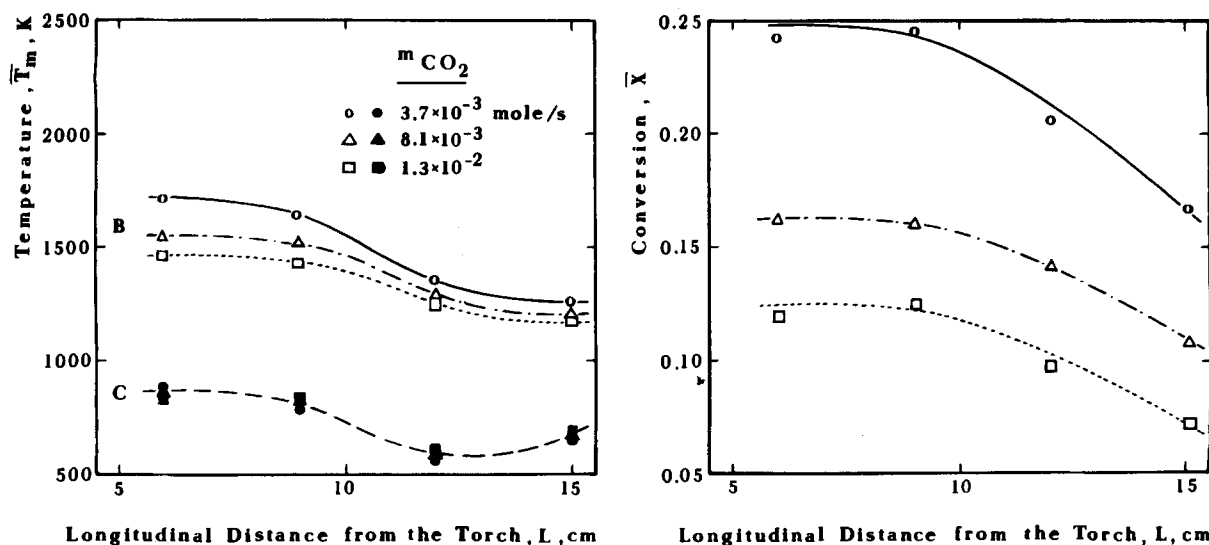


Figure 4. Averaged longitudinal temperature and conversion distributions.

TABLE 1. AVERAGED QUENCHING RATES, $\bar{W} \times 10^{-4}$, K/s

m_{CO_2} mol/s	Mixing Point-A	Section A-B	B-C	C-D
3.7×10^{-3}	7.98 ± 3.10	2.51 ± 1.88	318 ± 135	38.6 ± 28.7
8.1×10^{-3}	3.36 ± 2.32	2.46 ± 1.21	307 ± 99	47.6 ± 21.8
1.3×10^{-2}	2.66 ± 2.02	2.27 ± 0.95	314 ± 81	72.9 ± 19.7

$$W = 1.61 \times 10^2 (T_I - T_{II})^2 [m_{\text{Ar}} + m_{\text{CO}_2} (1 + 0.5\bar{X})] / \ln(T_I/T_{II}) \quad (4)$$

for the probe's channel. The results of calculations, averaged for different L distance are collected in Table 1.

Quenching rates in quartz tube are relatively small as a result of its heat-insulating character. Reasonably, the highest rates were found in probe's channel, especially in B-C section. The results ($\bar{W} > 3 \times 10^6$ K/s) are close to those of Sundstrom and De Michiell (1971) for plasma surface cooling. It should be stressed, that according to the theoretical consideration of Butylkin et al. (1979) the quenching rate should reach the value of 10^7 K/s to prevent the reverse reaction. Such quenching rates can be achieved as a result of a hot gas stream mixing with a colder one.

Polak (1965) has calculated the time of Maxwellization for the turbulent mixing of a plasma jet with cold gas and an order of magnitude of 10^{-8} s was obtained. Thus, for a very rapid mixing of reactants and establishing of quasiequilibrium it seems allowable to assume that the reaction is limited by normal decomposition kinetics and one can then apply classical kinetics and thermodynamics to the system. For such considerations it is necessary to know both reaction temperature and time. Holmen et al. (1976) noted that for high-temperature flow reactors it is difficult to find real reaction temperature.

In this work the T_r value was estimated on the base of both calculated, T_b , and measured, \bar{T}_m , temperatures according to the Borysowski (1976) approach. It was assumed also, that velocity profiles were proportional to the temperature ones (Katta et al., 1973).

Calculated equilibrium and experimental fractional conversion vs. reaction temperature are compared in Figure 5. Some differences may be attributed to the method of T_r estimation. It should be stressed, however, that even in quasiequilibrium systems one can find some deviations from thermal equilibrium (Kurochkin et al., 1978).

For the overall rate constant of reaction 1, the equation

$$k = C_{\text{CO}}/tC_{\text{CO}_2}C_{\text{Ar}} \quad (5)$$

has been used, assuming (according to the results in Table 1), that decomposition reaction is interrupted at the probe's inlet. For the reactor parameters characteristic of the experimental system Eq.

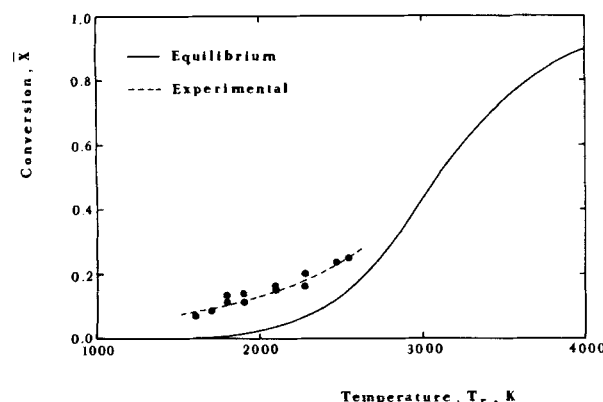


Figure 5. Conversion degree vs. temperature for the reaction $\text{CO}_2 \rightarrow \text{CO} + 0.5\text{O}_2$.

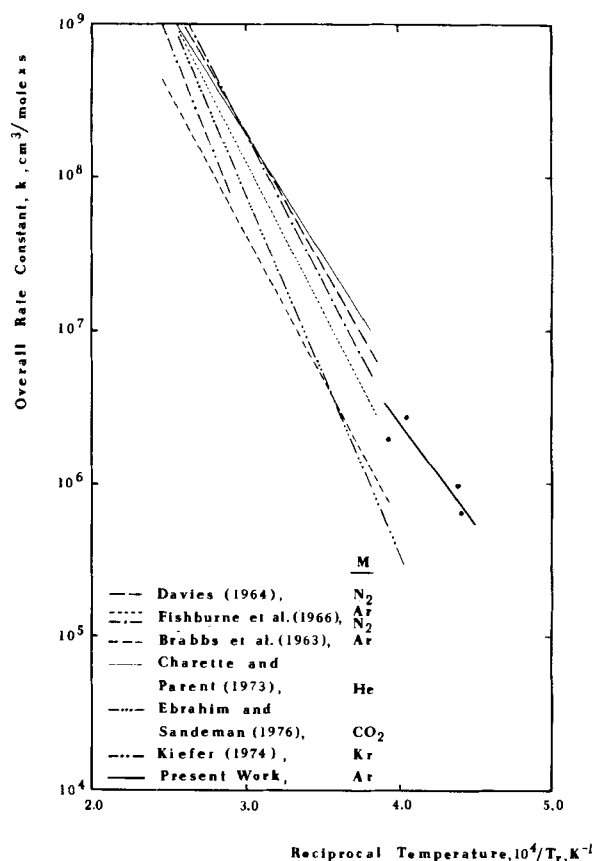


Figure 6. Arrhenius plot for reaction rate constant.

5 takes the form:

$$k = 3.82 \times 10^2 \bar{X} T_r^2 [m_{\text{Ar}} + m_{\text{CO}_2} (1 + 0.5\bar{X})]^2 / m_{\text{Ar}} L \quad (6)$$

The results of calculations (as an example, for $m_{\text{CO}_2} = 3.7 \times 10^{-3}$ mol/s) are close to those of other works (Figure 6). Over the reaction temperature range of the experiments, an activation energy $E_a = 240.7 \pm 0.5 RT$ kJ/mol gives the final Arrhenius equation

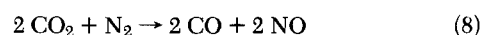
$$k = 5 \times 10^9 T^{1/2} \exp(-240.7/RT) \quad (7)$$

This activation energy was very close to the E_a value reported earlier by Charette and Parent (1973).

An effective energy consumption as low as about 1.5 MJ/mol CO was reached in this work, contrary to the 10 MJ/mol CO value reported by Charette and Parent (1973). With regard to energy efficiency the very high frequency discharge (Legasov et al., 1977) seems to be better, but capacity and limited, at the time, power of such a reactors decreases their applicability.

Further measurements will be made at higher arc discharge power, where it will be possible to determine reaction temperatures with a spectroscopic method. Some preliminary qualitative spectroscopic studies of the mixing zone (Figure 1) under high power conditions revealed the strong CI line at 2,478.65 Å corresponding to the $2p^2\ ^1S \rightarrow 3s\ ^1P^0$ transition. This proves that carbon dioxide undergoes complete decomposition in the hottest zone. The oxidation processes should be taken into account in the process modelling and the quench rate seems to be the most important factor influencing a decomposition efficiency.

One should mention, that the decomposition of CO_2 in an active plasma according to the equation



seems to be promising and both energetically and economically favourable. The preliminary results (N_2 plasma) confirm this supposition; nitrogen oxides (up to a few vol. %) and carbon monoxide were identified in reaction products.

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I would like to thank Professor A. Szymański for his valuable comments on this paper.

NOTATION

C_i	= component concentration
C_p^t	= molar heat capacity at constant pressure
E	= plasma energy
E_a	= activation energy
ΔH_i^{298}	= molar enthalpy of component formation
k	= overall reaction rate constant
L	= distance between the plasma torch and the probe
L_{I-II}	= distance between the measuring zones I and II; the zones (by turns): mixing point, A,B
m_i	= molar flow of component
R	= quartz tube radius
t	= reaction time
t_{I-II}	= time of reactions flow between measuring zones I and II
T	= temperature
T_b	= bulk mean mass temperature calculated according to the equation:
$E = m_{Ar} C_p^{Ar} (T_b - 298) + \bar{X} m_{CO_2} (\Delta H_{CO}^{298} - \Delta H_{CO_2}^{298})$ $+ m_{CO_2} [(1 - \bar{X}) \int_{298}^T C_p^{CO_2} dT + \bar{X} \int_{298}^T C_p^{CO} dT$ $+ 0.5 \bar{X} \int_{298}^T C_p^{O_2} dT]$	
T_m	= measured temperature
\bar{T}_m	= averaged measured temperature
T_r	= estimated reaction temperature
$T_{I,II}$	= temperature in measuring zones I, II
W	= quenching rate
\bar{W}	= averaged quenching rate
X	= fractional conversion
\bar{X}	= averaged fractional conversion

Subscripts

i = component i

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