

Reaction Mechanism of Ethylene Oxide at Various Oxygen/Ethylene Oxide Ratios in an RF Cold Plasma Environment

Wei-Tung Liao^{1*}, Ta-Chin Wei², Lien-Te Hsieh³, Cheng-Hsien Tsai⁴, and Minliang Shih⁵

¹*Department of Chemical and Material Engineering, Southern Taiwan University of Technology, Tainan, Taiwan*

²*Department of Chemical Engineering, Chung-Yuan University, Chung Li, Taiwan*

³*Department of Environmental Engineering and Science, National Pingtung University of Science and Technology, Pingtung, Taiwan*

⁴*Department of Chemical and Material Engineering, National Kaohsiung University of Applied Sciences, Kaohsiung, Taiwan*

⁵*Department of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, Tainan, Taiwan*

Abstract

An innovative method was used to simulate ethylene oxide (EO) oxidation in an RF plasma reactor. The objective of this work was to simulate the stable species mole fraction profiles measured in a flowing plasma system at constant temperature and pressure. The mechanism involved participation of 36 species in 140 elementary reactions. Sensitivity analysis was also performed to identify the order of significance of reactions in the mechanism of the model's predictions. The results show that the main reactions for EO decomposition changed with a varying O₂/EO ratio in the plasma system. That is to say, the most important reaction to the O₂/EO ratio of zero was the electron dissociation reaction of EO, $C_2H_4O + e^- \rightarrow CH_3CHO + e^-$. While, the most influential reaction for EO decomposition at O₂/EO ratio of 5.0 was the formation reaction of HO₂, which forms OH radicals, then enhances the decomposition of C₂H₄O by the reaction, $C_2H_4O + OH = C_2H_3O + H_2O$.

Keywords: ethylene oxide, plasma, radio-frequency (RF), reaction mechanism

* Corresponding author. Tel: 886-6-2533131ext 3700; 3722 ; Fax: 886-6-2425741

E-mail address: <mailto:wtliao@mail.stut.edu.tw>

INTRODUCTION

Ethylene oxide (EO) is widely used in chemical plants and hospitals to synthesize chemical intermediates and sterilize contaminated instruments. Controlling EO emission is of great importance, since it can be emitted into the environment through processing and ventilation of sterilization equipment, causing exposure risks to humans through the inhalation of polluted air. In a previous study (Liao et al., 2001), an RF plasma reactor with glow discharge was used to decompose EO-containing gas. The effects of plasma operational parameters for the EO decomposition, the profile of final products, and the fraction of total-carbon converted into CO₂ and CO were investigated in an EO/O₂/Ar plasma system. And the O₂/EO ratio, varying from 0 to 5, was chosen to represent the reaction conditions of oxygen-lean and oxygen-rich, and to see how oxygen influences the product profile in the EO/O₂/Ar plasma system. According to these results, the amount of oxygen needed for proceeding a suitable plasma reaction can be chosen, while the EO is drawn out from a closed reaction system, or a sterilization equipment.

Various types of plasma models have been proposed to provide an interpretation of diagnostic measurements and to understand the effects of operating parameters (Lister, 1992; Meyyappan and Govindan, 1995; Bose et al., 1999). Basic components for a complete plasma model should include: 1) an electric model describing discharge physics for charged species; 2) a plasma chemistry model, including fluid flow; and 3) a surface model, describing reactions at the substrate and chamber wall. While plasmas of gas mixtures are currently used in numerous industrial applications, modeling studies usually focus on plasma of a single gas. Few modeling studies of mixed-gas plasmas exist due to their complexity.

This paper describes an innovative method used to simulate the reaction mechanism of EO in the study of Liao et al (Liao et al., 2001). The mechanism involves 36 species in 140 elementary reactions. The objective of our work was to simulate the stable species mole fraction profiles measured in flowing plasma system at constant temperature and pressure. The Boltzmann equation was solved first to calculate the electron energy distribution function (EEDF). Mass and energy conservation equations were then solved to calculate the electron temperature and electron density as a function of feed composition. Combining the neutral reactions (Pitz and Westbrook, 1986; Dagaut et al., 1996) with the electron-neutral reactions, we constructed a complete mechanism for EO decomposition in the RF plasma reactor. By applying this mechanism and running the CHEMKIN II package (Kee et al., 1993), we obtained the calculated concentrations of products in the plasma reactor outlet. To test the accuracy of the model, the calculated results were compared with experimental measurements taken from literature (Liao et al., 2001). Via the sensitivity analysis by using SENKIN II program (Lutz et al., 1992), we identified the rank order of significance of reaction in the mechanism.

NUMERICAL METHODOLOGY

PLASMA MODEL

The plasma model includes three parts described as model assumption, charged species model and neutral species model.

MODEL ASSUMPTION

The reactor used in this study is a cylinder-type RF power supply reactor. In the operational range of this experiment, the species and their behavior in the plasma are assumed as follows. The species in the EO/O₂/Ar plasma will include charged species, neutral radicals and stable molecules.

- A. In the plasma reactor, the ambipolar diffusion velocity of charged species is higher than that of convection velocity, and the ion-electron recombination in plasma volume is negligible. Therefore, the electron density distribution in cylindrical plasma of radius R and length L is:

$$n_e(r, z) = n_{e0} \sin(\pi z/L) J_0(2.405 r/R)$$

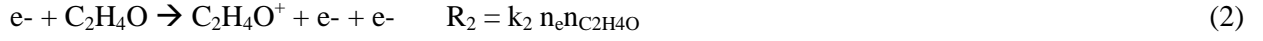
where J_0 is the zero-order Bessel function, and n_{e0} is the maximum electron density along the axis of the plasma (Roth, 1995). The average value of electron density distribution is used in the model to calculate the electron-neutral reaction rate.

- B. The convection velocity of neutral species is higher than that of the diffusion velocity; therefore, the neutral species in the plasma reactor can be assumed as plug flow reactor (PFR). In this model, the concentration of neutral species in the plasma reactor is a function of the position in the axis of reactor length.
- C. This plasma reactor is an isothermal reactor, both gas and electron temperatures are homogeneous.

CHARGED SPECIES MODEL

In this model, both mass and energy balances of charged species will be used to calculate the electron temperature (T_e) and electron density (n_e). Both T_e and n_e will be used for the calculation of reaction rate constant of electrons.

In the case of EO/O₂/Ar plasma, the charged species in this model will be Ar⁺, C₂H₄O⁺ and O₂⁺ ions and electron. Their reactions of formation are as follows.



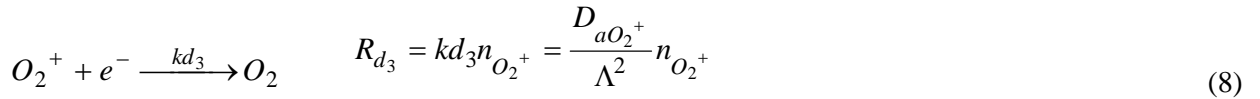
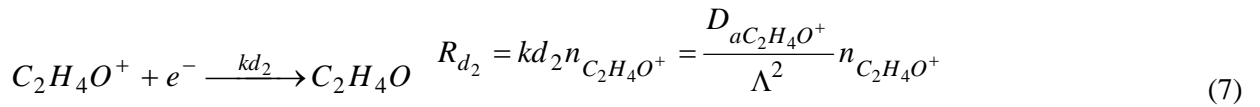
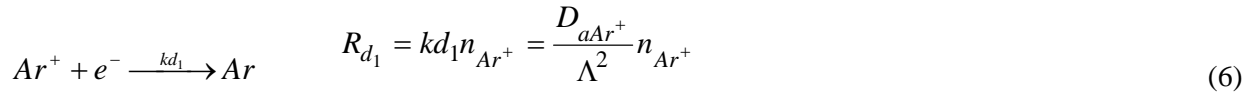
Therefore, the formation rate of electrons is as follows.

$$R_{ion} = R_1 + R_2 + R_3 = (\sum k_j f_j) n_e n_{Total} = k_{ion} n_e n_{Total} \quad (4)$$

where f_j is the mole fraction of component “j” in the inlet gaseous mixture.

$$n_{Total} = n_{Ar} + n_{C_2H_4O} + n_{O_2} \quad (5)$$

After formation, the positive ions will diffuse to the sheath in both radial and axial directions by ambipolar diffusion and then be neutralized by electrons (Lieberman and Lichtenburg, 1994; Roth, 1995).



Therefore, the consumption rate of electron is as follows:

$$R_d = R_{d_1} + R_{d_2} + R_{d_3} = \frac{D_{aa}}{\Lambda^2} n_{total \ ion} \quad (9)$$

$$D_{aa} = \mu_a \frac{P_{stp}}{P} \frac{T_g}{T_{stp}} \frac{kTe}{e} \quad (10)$$

$$\frac{1}{\Lambda^2} = \frac{1}{(R/2.405)^2} + \frac{1}{(L/\pi)^2} \quad (11)$$

$$\mu_a = \sum \mu_{ion} f_{ion} \quad (12)$$

$$\mu_{ion} = 14.74 (M_{ion})^{-0.5} \quad (13)$$

where R_d is diffusion rate of total positive ions; D_{aa} is the apparent ambipolar diffusivity; Λ is the characteristic diffusion length; P is operational pressure; P_{stp} is the pressure in standard conditions; T_{stp} is temperature in standard conditions; R is the radius of a cylinder-type reactor; L is plasma length; μ_a is apparent reduced mobility [$\text{cm}^2/(\text{sV})$]; n_{ion} is density of a certain ion in the plasma reactor; f_{ion} is mole fraction of a certain ion among total ions; M_{ion} is the molecular weight of a certain ion [amu].

In the steady state, $R_i=R_d$, the plasma is electrically neutral; therefore $n_e=n_{Total\ ion}$. Then

$$k_{ion} \frac{P}{RT_g} = \frac{D_{aa}}{\Lambda^2} \quad (14)$$

and,

$$k_0 e^{-E_a/T_e} \frac{P}{RT_g} = \mu_a \frac{P_{stp}}{P} \frac{T_g}{T_{stp}} T_e \left[\frac{1}{(R/2.405)^2} + \frac{1}{(L/\pi)^2} \right] \quad (15)$$

The k_0 (frequency factor) and E_a (apparent threshold energy) are calculated from the electron-impact-ionization of mixed feeding gas by Arrhenius plot (details in Section 2-1-3). Knowing k_0 , E_a , P , T_g , μ_a , R and L , we can calculate the electron temperature T_e .

In the RF plasma, when the operational pressure is between 10 and 30 torr, the electron temperature is much higher than the gas temperature. The gas temperature at the outlet of the plasma reactor was measured and used as the input parameter for this model. Also, we obtained the electron temperature by using the electron mass balance. Therefore, we can find the electron density (n_e) by an energy balance equation as follows.

$$0 = \beta P_{RF} - P_{ev} \quad (16)$$

β is the fraction of total input power absorbed by the plasma reactor. P_{RF} is the applied RF power and P_{ev} is the energy consumption rate of electron due to the electron-neutral collision.

In the plasma reactor, the collision between electron and neutral gas molecule can be divided into elastic and non-elastic collision. The non-elastic collision included ionization, dissociation and vibrational excitation reactions, etc. Therefore, the energy consumption rate in the plasma reactor can be expressed as follows.

$$P_{RF} = P_{ela} + P_{ion} + P_{dis} + P_{vib} = n_e (P'_{ela} + P'_{ion} + P'_{dis} + P'_{vib}) \quad (17)$$

where P'_i is the energy consumption rate of electrons during the “ i ” collision.

Bolsig software (Wei et al., 2000; Chen et al., 1999) can find the electron energy distribution function (EEDF) and the energy consumption of unit electrons at different types of collision reactions, as well as the collision frequency at different E/N values.

NEUTRAL SPECIES MODEL

When the EO/O₂/Ar mixing gas enters the plasma zone of the reactor, it can form neutral species such as free radicals and stable molecules. The composition of gas stream in the plasma zone will vary with the length in the gas flow direction. If we neglect the diffusion phenomenon of gas molecules, the neutral species can be described by using the PFR model.

$$\frac{1}{A} \frac{dF_i}{dZ} = \sum_j \nu_{ij} R_{ij} \quad (18)$$

where F_i is the molar flux of “ i ” species through a certain reference cross section of reactor; Z is the axial coordinate of cylinder-type reactor; A is the cross section of cylinder-type reactor; ν_{ij} is the stoichiometric coefficient of “ i ” species in the “ j ” reaction equation; R_{ij} is the reaction rate of “ i ” species in the “ j ” reaction equation

The distribution of electron energy in the plasma reactor can be calculated by Bolsig software as a function of E/N (reduced field; E is the electric field and N is the neutral density). After EEDF are calculated by running Bolsig software, the rate constants of electron-neutral reactions are obtained by calculating the following equation.

$$k = \int_0^{\infty} \left(\frac{2\varepsilon}{m} \right)^{\frac{1}{2}} \sigma(\varepsilon) f(\varepsilon) d\varepsilon \quad (19)$$

where k is the rate constant of electron reaction; ε is the electron energy; $\left(\frac{2\varepsilon}{m} \right)^{\frac{1}{2}}$ is the velocity of electrons; $\sigma(\varepsilon)$ is the distribution function of the cross section; and $f(\varepsilon)$ is the distribution function of electron energy.

For each electron-neutral reaction, the dependence of rate constant on electron temperature is fitted to the Arrhenius form ($k=k_0e^{-Ea/Te}$).

Modeling Description

The fundamental simulation for neutral reaction in the plasma reactor is based on the following principles (Kee et al., 1993): 1) Thermochemical theory; 2) Reaction kinetics, including Transition State Theory; and 3) The proper and accurate thermodynamic data.

The mechanism of the elementary reactions set describing the decomposition of EO are presented in this paper. This elementary reactions set consists of 140 elementary reactions and the available data obtained from previous references (Pitz and Westbrook, 1986; Dagaut et al., 1996). The rate parameters

containing three Arrhenius coefficients (pre-exponential factor, A; temperature exponent, n; and activation energy, Ea) for the forward reaction paths are also based on those studies. Reverse reaction rates are calculated from a detailed balancing between the forward and reverse rates through the use of the equilibrium constant. In all cases, rate parameters are consistent with reaction thermodynamics.

Combining these neutral reactions with the previous electron reactions, we can construct a complete mechanism for EO decomposition in the plasma reactor. Calculations can be conducted assuming a system where the pressure and temperature are constant, and performed over a cylindrical domain with a diameter of 4.14 cm and a height of plasma length. The pressure of the reaction in the RF plasma reactor was set to 20 Torr and the initial temperature was set as the gas temperature, which is measured at the plasma reactor's outlet.

SENSITIVITY ANALYSIS

The major reaction channels responsible for the decomposition and formation of species were identified by sensitivity analysis. Sensitivity analysis involves quantitative information in how the rate coefficients affect the reaction conditions. Sandia SENKIN computer code was used for the calculation of sensitivity coefficients (Dean et al., 1991). Reaction pathways responsible for the decomposition and formation of species were then determined from the calculations of individual reaction rates and first-order normalized sensitivity coefficients (W_{ij}). The W_{ij} 's were defined as the following:

$$W_{ij} = (A_i/Z_j)[\partial Z_j/\partial A_i] \quad (20)$$

where Z_j is the concentration of species j, and A_i is the pre-exponential constant of the forward branch of the i th elementary reaction (Won and Bozzelli, 1992).

RESULTS AND DISCUSSION

KINETIC PARAMETERS OF ELECTRON-NEUTRAL REACTIONS

In this study, the rate constants were obtained in two ways: 1) by estimation using the threshold energy, maximum cross-section and averaged electron temperature; and 2) by calculation integrating the total cross-section function and the electron energy distribution function.

The total cross-section for the dissociation reaction of CH_4 collided with electrons can be found in the Winters et al. (1975, 1979). By applying the calculation process described in the previous section, we get

the total dissociation rate constant. Then, the rate ratio of three following CH₄ dissociation reactions suggested by Fan et al. (1999) was taken.



This implies that the rate constant ratio of the above three reactions are 2.5:2.5:1. By using this ratio, individual rate constants can be obtained.

Table 1. The elementary reaction mechanism for the EO/O₂/Ar plasma.

No.	Reaction equation	A	n	Ea	Reference
1	$\text{e}^- + \text{C}_2\text{H}_4\text{O} \Rightarrow \text{CH}_3\text{CHO} + \text{e}^-$	(5)	—	—	Est
2	$\text{e}^- + \text{CH}_3\text{CHO} \Rightarrow \text{CH}_3 + \text{CHO} + \text{e}^-$	(5)	—	—	Est
3	$\text{e}^- + \text{O}_2 \Rightarrow \text{O} + \text{O} + \text{e}^-$	(6)	—	—	Cal
4	$\text{e}^- + \text{H}_2 \Rightarrow \text{H} + \text{H} + \text{e}^-$	(6)	—	—	Cal
5	$\text{e}^- + \text{H}_2\text{O} \Rightarrow \text{H} + \text{OH} + \text{e}^-$	(6)	—	—	Cal
6	$\text{e}^- + \text{CH}_4 \Rightarrow \text{CH}_3 + \text{H} + \text{e}^-$	(6)	—	—	Cal
7	$\text{e}^- + \text{CH}_4 \Rightarrow \text{CH}_2 + \text{H}_2 + \text{e}^-$	(6)	—	—	Cal
8	$\text{e}^- + \text{CH}_4 \Rightarrow \text{CH} + \text{H}_2 + \text{H} + \text{e}^-$	(6)	—	—	Cal
9	$\text{e}^- + \text{C}_2\text{H}_4 \Rightarrow \text{C}_2\text{H}_3 + \text{H} + \text{e}^-$	(6)	—	—	Cal
10	$\text{e}^- + \text{C}_2\text{H}_4 \Rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{e}^-$	(6)	—	—	Cal
11	$\text{e}^- + \text{C}_2\text{H}_6 \Rightarrow \text{C}_2\text{H}_5 + \text{H} + \text{e}^-$	(6)	—	—	Cal
12	$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	1.66E+15	0	-1000	Pitz and Westbrook, 1986
13	$\text{H} + \text{O}_2 = \text{OH} + \text{O}$	5.13E+16	-0.8	16510	Pitz and Westbrook, 1986
14	$\text{H}_2 + \text{M} = \text{H} + \text{H} + \text{M}$	2.19E+14	0	96000	Pitz and Westbrook, 1986
15	$\text{H}_2 + \text{O} = \text{H} + \text{OH}$	1.82E+10	1	8900	Pitz and Westbrook, 1986
16	$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$	5.01E+13	0	1000	Pitz and Westbrook, 1986
17	$\text{HO}_2 + \text{O} = \text{OH} + \text{O}_2$	5.01E+13	0	1000	Pitz and Westbrook, 1986
18	$\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$	2.51E+14	0	1900	Pitz and Westbrook, 1986
19	$\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$	2.51E+13	0	700	Pitz and Westbrook, 1986
20	$\text{H}_2\text{O} + \text{H} = \text{H}_2 + \text{OH}$	9.55E+13	0	20300	Pitz and Westbrook, 1986
21	$\text{H}_2\text{O} + \text{O} = \text{OH} + \text{OH}$	6.76E+13	0	18350	Pitz and Westbrook, 1986
22	$\text{H}_2\text{O} + \text{M} = \text{H} + \text{OH} + \text{M}$	2.19E+16	0	105000	Pitz and Westbrook, 1986
23	$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$	1.20E+17	0	45474.1	Pitz and Westbrook, 1986

24	$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	1.00E+13	0	1800	Pitz and Westbrook, 1986
25	$\text{H}_2\text{O}_2 + \text{O}_2 = \text{HO}_2 + \text{HO}_2$	3.98E+13	0	42640	Pitz and Westbrook, 1986
26	$\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$	1.70E+12	0	3750	Pitz and Westbrook, 1986
27	$\text{HCCO} + \text{OH} = \text{CHO} + \text{CHO}$	1.00E+13	0	0	Pitz and Westbrook, 1986
28	$\text{HCCO} + \text{H} = \text{CH}_2 + \text{CO}$	5.01E+13	0	0	Pitz and Westbrook, 1986
29	$\text{HCCO} + \text{O} = \text{CHO} + \text{CO}$	3.39E+13	0	2000	Pitz and Westbrook, 1986
30	$\text{O} + \text{H} + \text{M} = \text{OH} + \text{M}$	1.00E+16	0	0	Pitz and Westbrook, 1986
31	$\text{O}_2 + \text{M} = \text{O} + \text{O} + \text{M}$	5.13E+15	0	115000	Pitz and Westbrook, 1986
32	$\text{C} + \text{O}_2 = \text{CO} + \text{O}$	2.00E+13	0	0	Pitz and Westbrook, 1986
33	$\text{C} + \text{CH}_2 = \text{C}_2\text{H} + \text{H}$	5.00E+13	0	0	Pitz and Westbrook, 1986
34	$\text{C} + \text{OH} = \text{CO} + \text{H}$	5.00E+13	0.0	0.0	Pitz and Westbrook, 1986
35	$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$	1.51E+14	0	23650	Pitz and Westbrook, 1986
36	$\text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M}$	5.89E+15	0	4100	Pitz and Westbrook, 1986
37	$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	1.50E+07	1.3	-770	Pitz and Westbrook, 1986
38	$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	3.16E+11	0	37600	Pitz and Westbrook, 1986
39	$\text{CH} + \text{O}_2 = \text{CO} + \text{OH}$	1.35E+11	0.67	25700	Pitz and Westbrook, 1986
40	$\text{CH} + \text{M} = \text{C} + \text{H} + \text{M}$	1.90E+14	0	0	Dagaut et al., 1996
41	$\text{CH} + \text{O}_2 = \text{CHO} + \text{O}$	1.00E+13	0	0	Pitz and Westbrook, 1986
42	$\text{CH} + \text{OH} = \text{C} + \text{H}_2\text{O}$	4.00E+07	2	3000	Dagaut et al., 1996
43	$\text{CH} + \text{H} = \text{C} + \text{H}_2$	1.50E+14	0	0	Pitz and Westbrook, 1986
44	$\text{CHO} + \text{O} = \text{CO} + \text{OH}$	1.00E+14	0	0	Pitz and Westbrook, 1986
45	$\text{CHO} + \text{O}_2 = \text{CO} + \text{HO}_2$	3.02E+12	0	0	Pitz and Westbrook, 1986
46	$\text{CHO} + \text{M} = \text{H} + \text{CO} + \text{M}$	1.45E+14	0	19000	Pitz and Westbrook, 1986
47	$\text{CHO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	1.00E+14	0	0	Pitz and Westbrook, 1986
48	$\text{CHO} + \text{H} = \text{CO} + \text{H}_2$	2.00E+14	0	0	Pitz and Westbrook, 1986
49	$\text{CHO} + \text{HO}_2 = \text{CH}_2\text{O} + \text{O}_2$	1.00E+14	0	3000	Pitz and Westbrook, 1986
50	$\text{CH}_2 + \text{O}_2 = \text{CHO} + \text{OH}$	1.00E+14	0	3700	Pitz and Westbrook, 1986
51	$\text{CH}_2 + \text{O} = \text{CH} + \text{OH}$	1.91E+11	0.68	25000	Pitz and Westbrook, 1986
52	$\text{CH}_2 + \text{OH} = \text{CH} + \text{H}_2\text{O}$	2.69E+11	0.67	25700	Pitz and Westbrook, 1986
53	$\text{CH}_2 + \text{H} = \text{CH} + \text{H}_2$	2.69E+11	0.67	25700	Pitz and Westbrook, 1986
54	$\text{CH}_2 + \text{M} = \text{C} + \text{H}_2 + \text{M}$	1.30E+14	0	59000	Pitz and Westbrook, 1986
55	$\text{CH}_2\text{O} + \text{H} = \text{CHO} + \text{H}_2$	3.31E+14	0	10500	Pitz and Westbrook, 1986
56	$\text{CH}_2\text{O} + \text{O} = \text{CHO} + \text{OH}$	5.01E+13	0	4600	Pitz and Westbrook, 1986
57	$\text{CH}_2\text{O} + \text{CH}_2 = \text{C}_2\text{H}_4 + \text{O}$	3.02E+12	0	15680	Pitz and Westbrook, 1986
58	$\text{CH}_2\text{O} + \text{M} = \text{CHO} + \text{H} + \text{M}$	3.31E+16	0	81000	Pitz and Westbrook, 1986
59	$\text{CH}_2\text{O} + \text{OH} = \text{CHO} + \text{H}_2\text{O}$	7.59E+12	0	170	Pitz and Westbrook, 1986

60	$\text{CH}_2\text{O}+\text{HO}_2=\text{CHO}+\text{H}_2\text{O}_2$	2.00E+11	0	8000	Pitz and Westbrook, 1986
61	$\text{CH}_2\text{O}+\text{H}+\text{M}=\text{CH}_3\text{O}+\text{M}$	1.00E+09	1	-2560	Pitz and Westbrook, 1986
62	$\text{CH}_2\text{O}+\text{CH}_3=\text{CH}_4+\text{CHO}$	1.00E+10	0.5	6000	Pitz and Westbrook, 1986
63	$\text{CH}_2\text{OH}+\text{M}=\text{CH}_2\text{O}+\text{H}+\text{M}$	2.51E+13	0	29000	Pitz and Westbrook, 1986
64	$\text{CH}_2\text{OH}+\text{O}_2=\text{CH}_2\text{O}+\text{HO}_2$	8.32E+11	0	0	Pitz and Westbrook, 1986
65	$\text{CH}_3+\text{CH}_3\text{CHO}=\text{CH}_4+\text{CH}_3\text{CO}$	1.74E+12	0	8440	Pitz and Westbrook, 1986
66	$\text{CH}_3+\text{CH}_3+\text{M}=\text{C}_2\text{H}_6+\text{M}$	2.10E+20	0	0	Pitz and Westbrook, 1986
67	$\text{CH}_3+\text{CO}+\text{M}=\text{CH}_3\text{CO}+\text{M}$	1.58E+11	0	5970	Pitz and Westbrook, 1986
68	$\text{CH}_3+\text{O}=\text{CH}_2\text{O}+\text{H}$	1.29E+14	0	2000	Pitz and Westbrook, 1986
69	$\text{CH}_3+\text{H}+\text{M}=\text{CH}_4+\text{M}$	2.90E+19	0	0	Pitz and Westbrook, 1986
70	$\text{CH}_3+\text{OH}=\text{CH}_2\text{O}+\text{H}_2$	3.98E+12	0	0	Pitz and Westbrook, 1986
71	$\text{CH}_3+\text{H}_2=\text{CH}_4+\text{H}$	4.79E+12	0	11430	Pitz and Westbrook, 1986
72	$\text{CH}_3+\text{C}=\text{C}_2\text{H}_2+\text{H}$	5.00E+13	0	0	Pitz and Westbrook, 1986
73	$\text{CH}_3+\text{HO}_2=\text{CH}_3\text{O}+\text{OH}$	3.24E+13	0	0	Pitz and Westbrook, 1986
74	$\text{CH}_3+\text{O}_2=\text{CH}_3\text{O}+\text{O}$	4.79E+13	0	29000	Pitz and Westbrook, 1986
75	$\text{CH}_3+\text{CH}_2\text{O}=\text{C}_2\text{H}_4+\text{OH}$	6.03E+11	0	16480	Pitz and Westbrook, 1986
76	$\text{CH}_3\text{O}+\text{CH}_2\text{O}=\text{CH}_3\text{OH}+\text{CHO}$	6.03E+11	0	3300	Pitz and Westbrook, 1986
77	$\text{CH}_3\text{O}+\text{O}_2=\text{CH}_2\text{O}+\text{HO}_2$	7.59E+10	0	2700	Pitz and Westbrook, 1986
78	$\text{CH}_3\text{OH}+\text{M}=\text{CH}_3+\text{OH}+\text{M}$	3.02E+18	0	80000	Pitz and Westbrook, 1986
79	$\text{CH}_3\text{OH}+\text{OH}=\text{CH}_2\text{OH}+\text{H}_2\text{O}$	3.98E+12	0	1370	Pitz and Westbrook, 1986
80	$\text{CH}_3\text{OH}+\text{O}=\text{CH}_2\text{OH}+\text{OH}$	1.70E+12	0	2290	Pitz and Westbrook, 1986
81	$\text{CH}_3\text{OH}+\text{H}=\text{CH}_2\text{OH}+\text{H}_2$	3.02E+13	0	7000	Pitz and Westbrook, 1986
82	$\text{CH}_3\text{OH}+\text{CH}_3=\text{CH}_2\text{OH}+\text{CH}_4$	1.82E+11	0	9800	Pitz and Westbrook, 1986
83	$\text{CH}_3\text{OH}+\text{HO}_2=\text{CH}_2\text{OH}+\text{H}_2\text{O}_2$	6.31E+12	0	19360	Pitz and Westbrook, 1986
84	$\text{CH}_3\text{OH}+\text{H}=\text{CH}_3+\text{H}_2\text{O}$	5.25E+12	0	5340	Pitz and Westbrook, 1986
85	$\text{CH}_3\text{CHO}+\text{CHO}=\text{CH}_3\text{CO}+\text{CH}_2\text{O}$	7.800E+13	0.0	8440	Dagaut et al., 1996
86	$\text{CH}_4+\text{OH}=\text{CH}_3+\text{H}_2\text{O}$	3.47E+03	3.08	2000	Pitz and Westbrook, 1986
87	$\text{CH}_4+\text{O}=\text{CH}_3+\text{OH}$	1.62E+06	2.3	7094	Dagaut et al., 1996
88	$\text{CH}_4+\text{CO}=\text{CH}_3+\text{CHO}$	5.13E+13	0.5	90470	Pitz and Westbrook, 1986
89	$\text{CH}_4+\text{O}_2=\text{CH}_3+\text{HO}_2$	7.59E+13	0	58590	Pitz and Westbrook, 1986
90	$\text{CH}_4+\text{HO}_2=\text{CH}_3+\text{H}_2\text{O}_2$	2.00E+13	0	18000	Pitz and Westbrook, 1986
91	$\text{CH}_2\text{CO}+\text{H}=\text{CH}_3+\text{CO}$	1.10E+13	0	3400	Pitz and Westbrook, 1986
92	$\text{CH}_2\text{CO}+\text{O}=\text{CHO}+\text{CHO}$	1.00E+13	0	2400	Pitz and Westbrook, 1986
93	$\text{CH}_2\text{CO}+\text{OH}=\text{CH}_2\text{O}+\text{CHO}$	2.82E+13	0	0	Pitz and Westbrook, 1986
94	$\text{CH}_2\text{CO}+\text{M}=\text{CH}_2+\text{CO}+\text{M}$	2.00E+16	0	60000	Pitz and Westbrook, 1986
95	$\text{CH}_2\text{CO}+\text{O}=\text{HCCO}+\text{OH}$	5.01E+13	0	8000	Pitz and Westbrook, 1986

96	$\text{CH}_2\text{CO}+\text{OH}=\text{HCCO}+\text{H}_2\text{O}$	7.59E+12	0	3000	Pitz and Westbrook, 1986
97	$\text{CH}_2\text{CO}+\text{H}=\text{HCCO}+\text{H}_2$	7.59E+13	0	8000	Pitz and Westbrook, 1986
98	$\text{CH}_3\text{CHO}+\text{HO}_2=\text{CH}_3\text{CO}+\text{H}_2\text{O}_2$	1.700E+12	0.0	10700	Dagaut et al., 1996
99	$\text{CH}_3\text{CHO}+\text{OH}=\text{CH}_3\text{CO}+\text{H}_2\text{O}$	2.350E+10	0.73	-1113	Dagaut et al., 1996
100	$\text{CH}_3\text{CHO}+\text{O}_2=\text{CH}_3\text{CO}+\text{HO}_2$	2.000E+13	0.5	42200.0	Dagaut et al., 1996
101	$\text{CH}_3\text{CHO}+\text{O}=\text{CH}_3\text{CO}+\text{OH}$	5.01E+12	0	1790	Pitz and Westbrook, 1986
102	$\text{CH}_3\text{CHO}+\text{H}=\text{CH}_3\text{CO}+\text{H}_2$	3.98E+13	0	4200	Pitz and Westbrook, 1986
103	$\text{C}_2\text{H}+\text{H}+\text{M}=\text{C}_2\text{H}_2+\text{M}$	4.500E+29	-3.1	1433.0	Pitz and Westbrook, 1986
104	$\text{C}_2\text{H}+\text{H}_2=\text{C}_2\text{H}_2+\text{H}$	4.17E+13	0	13210	Pitz and Westbrook, 1986
105	$\text{C}_2\text{H}+\text{H}_2\text{O}=\text{C}_2\text{H}_2+\text{OH}$	5.37E+12	0	16360	Pitz and Westbrook, 1986
106	$\text{C}_2\text{H}+\text{OH}=\text{C}_2\text{H}_2+\text{O}$	2.95E+14	-0.6	910	Pitz and Westbrook, 1986
107	$\text{C}_2\text{H}+\text{O}_2=\text{CHO}+\text{CO}$	1.00E+13	0	7000	Pitz and Westbrook, 1986
108	$\text{C}_2\text{H}+\text{O}=\text{CO}+\text{CH}$	5.01E+13	0	0	Pitz and Westbrook, 1986
109	$\text{C}_2\text{H}+\text{C}_2\text{H}_2=\text{C}_2\text{H}_2+\text{H}$	3.98E+13	0	0	Pitz and Westbrook, 1986
110	$\text{C}_2\text{H}_2+\text{O}_2=\text{CHO}+\text{CHO}$	3.98E+12	0	28000	Pitz and Westbrook, 1986
111	$\text{C}_2\text{H}_2+\text{OH}=\text{CH}_2\text{CO}+\text{H}$	3.24E+11	0	200	Pitz and Westbrook, 1986
112	$\text{C}_2\text{H}_2+\text{HO}_2=\text{C}_2\text{H}_2+\text{O}_2$	1.00E+12	0	17870	Pitz and Westbrook, 1986
113	$\text{C}_2\text{H}_2+\text{O}=\text{CH}_2+\text{CO}$	6.76E+13	0	4000	Pitz and Westbrook, 1986
114	$\text{C}_2\text{H}_2+\text{O}=\text{HCCO}+\text{H}$	3.55E+04	2.7	1390	Pitz and Westbrook, 1986
115	$\text{C}_2\text{H}_2+\text{H}=\text{C}_2\text{H}_2+\text{H}_2$	2.00E+13	0	2500	Pitz and Westbrook, 1986
116	$\text{C}_2\text{H}_3+\text{M}=\text{C}_2\text{H}_2+\text{H}+\text{M}$	7.94E+14	0	31500	Pitz and Westbrook, 1986
117	$\text{C}_2\text{H}_3+\text{H}_2=\text{C}_2\text{H}_4+\text{H}$	1.74E+06	2	5110	Pitz and Westbrook, 1986
118	$\text{C}_2\text{H}_3\text{O}=\text{CH}_2\text{CO}+\text{H}$	1.60E+13	0	35000	Dagaut et al., 1996
119	$\text{C}_2\text{H}_3\text{O}=\text{CH}_3\text{CO}$	8.51E+14	0	14000	Dagaut et al., 1996
120	$\text{C}_2\text{H}_4+\text{M}=\text{C}_2\text{H}_2+\text{H}_2+\text{M}$	9.33E+16	0	77200	Pitz and Westbrook, 1986
121	$\text{C}_2\text{H}_4+\text{O}=\text{CH}_3+\text{CHO}$	3.31E+12	0	1130	Pitz and Westbrook, 1986
122	$\text{C}_2\text{H}_4+\text{CH}_3=\text{CH}_4+\text{C}_2\text{H}_3$	2.55E+00	2	2199	Pitz and Westbrook, 1986
123	$\text{C}_2\text{H}_4+\text{O}=\text{C}_2\text{H}_3+\text{OH}$	2.53E+13	0	4991.6	Pitz and Westbrook, 1986
124	$\text{C}_2\text{H}_4+\text{C}_2\text{H}_4=\text{C}_2\text{H}_5+\text{C}_2\text{H}_3$	5.01E+14	0	64700	Pitz and Westbrook, 1986
125	$\text{C}_2\text{H}_4+\text{OH}=\text{C}_2\text{H}_3+\text{H}_2\text{O}$	4.79E+12	0	1230	Pitz and Westbrook, 1986
126	$\text{C}_2\text{H}_4\text{O}+\text{O}_2=\text{C}_2\text{H}_3\text{O}+\text{HO}_2$	4.00E+13	0	61500	Dagaut et al., 1996
127	$\text{C}_2\text{H}_4\text{O}+\text{H}=\text{C}_2\text{H}_3\text{O}+\text{H}_2$	2.00E+13	0	8300	Dagaut et al., 1996
128	$\text{C}_2\text{H}_4\text{O}+\text{H}=\text{C}_2\text{H}_3+\text{H}_2\text{O}$	5.00E+09	0	5000	Dagaut et al., 1996
129	$\text{C}_2\text{H}_4\text{O}+\text{H}=\text{C}_2\text{H}_4+\text{OH}$	9.51E+10	0	5000	Dagaut et al., 1996
130	$\text{C}_2\text{H}_4\text{O}+\text{O}=\text{C}_2\text{H}_3\text{O}+\text{OH}$	1.91E+12	0	5250	Dagaut et al., 1996
131	$\text{C}_2\text{H}_4\text{O}+\text{OH}=\text{C}_2\text{H}_3\text{O}+\text{H}_2\text{O}$	4.79E+13	0	5955	Dagaut et al., 1996

132	$C_2H_4O+HO_2=C_2H_3O+H_2O_2$	4.00E+12	0	17000	Dagaut et al., 1996
133	$C_2H_4O+CH_3=CH_4+C_2H_3O$	1.07E+12	0	11830	Dagaut et al., 1996
134	$C_2H_5+M=C_2H_4+H+M$	2.00E+15	0	30000	Pitz and Westbrook, 1986
135	$C_2H_5+H=CH_3+CH_3$	3.16E+12	0	0	Pitz and Westbrook, 1986
136	$C_2H_5+O_2=C_2H_4+HO_2$	1.00E+12	0	5000	Pitz and Westbrook, 1986
137	$C_2H_6+CH_3=C_2H_5+CH_4$	5.50E-01	4	8280	Pitz and Westbrook, 1986
138	$C_2H_6+H=C_2H_5+H_2$	5.37E+02	3.5	5200	Pitz and Westbrook, 1986
139	$C_2H_6+OH=C_2H_5+H_2O$	8.71E+09	1.05	1810	Pitz and Westbrook, 1986
140	$C_2H_6+O=C_2H_5+OH$	1.12E+14	0	7850	Pitz and Westbrook, 1986

Note : (1) Reaction mechanism and rate constants expressed as: $k = A T^n \exp(-E_a / RT)$. (2) A unit = $cm^3/(mol \text{ sec})$ for bimolecular reactions, 1/sec for unimolecular reactions. s. (3) E_a unit = cal/mol. (4) T unit = k. (5) Est. = Estimated in this study. (6) Cal. = Calculation in this study.

Combining the neutral reactions (Pitz and Westbrook, 1986; Dagaut et al., 1996) with the electron-neutral reactions, we construct a complete mechanism, shown in Table 1, for EO decomposition in this RF plasma reactor. The rate constants of electron-neutral impact dissociation reactions at various O_2/EO ratios are shown in Table 2.

Table 2. The rate constants [$cm^3/(mol \text{ sec})$] of electron-neutral impact dissociation reactions at various O_2/EO ratios.

reaction no.	reaction	O_2/EO ratios					
		0	0.5	1.0	1.5	2.0	5.0
1	$e^-+C_2H_4O=>CH_3CHO+e^-$	5.98×10^{13}	1.12×10^{14}	7.22×10^{13}	1.03×10^{14}	1.17×10^{14}	2.17×10^{13}
2	$e^-+CH_3CHO=>CH_3+CHO+e^-$	5.98×10^{13}	1.12×10^{14}	7.22×10^{13}	1.03×10^{14}	1.17×10^{14}	2.17×10^{13}
3	$e^-+O_2=>O+O+e^-$	7.95×10^{14}	1.49×10^{15}	1.32×10^{15}	1.37×10^{15}	1.56×10^{15}	2.90×10^{14}
4	$e^-+H_2=>H+H+e^-$	2.21×10^{15}	4.13×10^{15}	2.65×10^{15}	3.79×10^{15}	4.17×10^{15}	8.01×10^{13}
5	$e^-+H_2O=>H+OH+e^-$	4.71×10^{13}	8.79×10^{13}	5.67×10^{13}	8.07×10^{13}	9.21×10^{13}	1.71×10^{13}
6	$e^-+CH_4=>CH_3+H+e^-$	3.74×10^{13}	2.20×10^{13}	1.18×10^{13}	9.45×10^{12}	6.44×10^{12}	5.99×10^{12}
7	$e^-+CH_4=>CH_2+H_2+e^-$	3.74×10^{13}	2.20×10^{13}	1.18×10^{13}	9.45×10^{12}	6.44×10^{12}	5.99×10^{12}
8	$e^-+CH_4=>CH+H_2+H+e^-$	1.49×10^{13}	8.79×10^{12}	4.71×10^{12}	3.78×10^{12}	2.58×10^{12}	2.40×10^{12}
9	$e^-+C_2H_4=>C_2H_3+H+e^-$	3.32×10^{13}	1.95×10^{13}	1.05×10^{13}	8.43×10^{12}	5.73×10^{12}	5.33×10^{12}
10	$e^-+C_2H_4=>C_2H_2+H_2+e^-$	1.33×10^{14}	7.83×10^{13}	4.19×10^{13}	3.36×10^{13}	2.29×10^{13}	2.13×10^{13}
11	$e^-+C_2H_6=>C_2H_5+H+e^-$	1.66×10^{14}	9.75×10^{13}	5.24×10^{13}	4.20×10^{13}	2.87×10^{13}	2.66×10^{13}

COMPARISON OF THE SIMULATED RESULTS WITH THE EXPERIMENTAL DATA

Calculations were conducted assuming a system where the pressure and temperature are constant, and were performed over a cylindrical domain with a diameter of 4.14 cm and a height of plasma length. The pressure of the reaction in the RF plasma reactor was set to 20 Torr and the initial temperature was set as the gas temperature, which was measured at the outlet of the plasma reactor. By applying the above mechanism and running the CHEMKIN II package (Kee et al., 1993), we obtained the calculated concentrations of residual reactant and products in the outlet of the plasma reactor.

Comparison of experimental and calculated decomposition fraction of EO for various EO/O₂ ratios are shown in Figure 1. It shows that the simulation results are in good agreement with the experimental data. Figure 2 shows the model prediction results of product concentrations. It also shows that the model prediction results agree well with the experimental results. Figure 2(b) shows the model predictions for carbon monoxide is overestimated at 0 of O₂/EO ratio. A possible reason for this overestimate of carbon monoxide is the lack of reactions in our mechanism to species of higher molecular weight, such as polyhydrocarbon species and soot. In this circumstance, the carbon contained in the reactant might lead to the formation of CO product. This is in agreement with predictions on polyaromatic compound formation (Stein and Fahr, 1985). At some high temperature levels in EO/Ar plasma decomposition, the radicals and unsaturated molecules begin to combine leading, ultimately, to soot or highly carbonized structures. Krestinin (2000) and others (Vuitton et al., 2001) think that the soot may be formed via the acetylene pathway; i.e. polyynes model and the diacetylene, C₄H₂, is recognized as a soot precursor. Without thermo data for polyynes, C_{2n}H₂, the model was not introduced in this work. However, the concentration of carbon monoxide between the experimental and modeled data was still within 18% of difference.

SENSITIVITY ANALYSIS

According to the sensitivity analysis method described, we can obtain the sequence of the sensitivity coefficients in the plasma reaction. In addition, the major reaction channels responsible for the decomposition and formation of species have been identified. Those results are presented below.

FIVE MOST IMPORTANT REACTIONS RELATED TO C₂H₄O IN THE EO/AR PLASMA SYSTEM

The most important five reactions involving the decomposition of C_2H_4O , in sequence, are shown in Table 3. Each sensitivity coefficient value, which is responsible for the corresponding reaction, follows each reaction. Table 3 also presents results from the sensitivity analysis on the model for the relative importance of C_2H_4O decomposition reactions in EO/Ar plasma system. Both equations of $C_2H_4O+e^- \Rightarrow CH_3CHO+e^-$ and $C_2H_4O+H=C_2H_3O+H_2$ with significant negative sensitivity coefficients are the most important decomposition reactions over the operation regime. In a whole view, Table 3 shows that those two reactions are the dominant decomposition paths for C_2H_4O in the condition in which no O_2 was added. However, both equations of $CH+H=C+H_2$ and $CH_3+H+M=CH_4+M$ with larger positive sensitivity coefficients will inhibit the decomposition of C_2H_4O . The reason is that the reactions $CH+H=C+H_2$ and $CH_3+H+M=CH_4+M$ will compete with H with the reaction $C_2H_4O+H=C_2H_3O+H_2$. So, enhancing the reactions of $CH+H=C+H_2$ and $CH_3+H+M=CH_4+M$ will weaken the C_2H_4O decomposition reaction $C_2H_4O+H=C_2H_3O+H_2$.

Table 3. The most important five reactions related to C_2H_4O in EO/Ar plasma.

Rank of sensitivity	Reaction equation	Sensitivity coefficient
1	$C_2H_4O+e^- \Rightarrow CH_3CHO+e^-$	-2.33E+00
2	$C_2H_4O+H=C_2H_3O+H_2$	-8.39E-01
3	$H_2+e^- \Rightarrow H+H+e^-$	-5.02E-01
4	$CH+H=C+H_2$	4.66E-01
5	$CH_3+H+M=CH_4+M$	4.11E-01

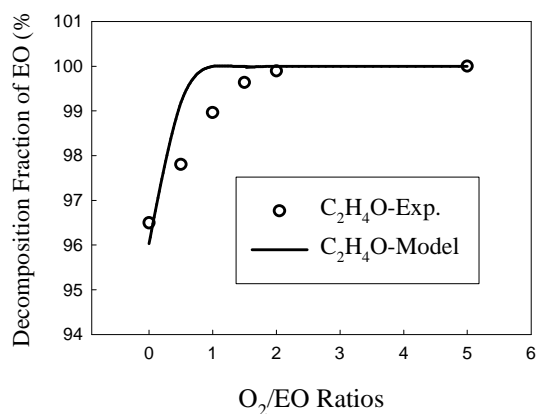


Figure 1. The comparison of calculated data with experimental data on the decomposition fraction of EO at various O_2/EO ratios (input power = 30 W; operational pressure = 20 torr; Eo feeding concentration = 2%; total gas flow rate = 100 sccm).

Table 4. The most important five reactions related to C₂H₄O in EO/O₂/Ar plasma.

Rank of sensitivity	Reaction equation	Sensitivity coefficient
1	$H+O_2+M=HO_2+M$	-5.29E-01
2	$O_2+e^- = O+O+e^-$	2.80E-01
3	$C_2H_4O+H=C_2H_3O+H_2$	-1.84E-01
4	$C_2H_4O+OH=C_2H_3O+H_2O$	-9.60E-02
5	$O+H+M=OH+M$	-9.09E-02

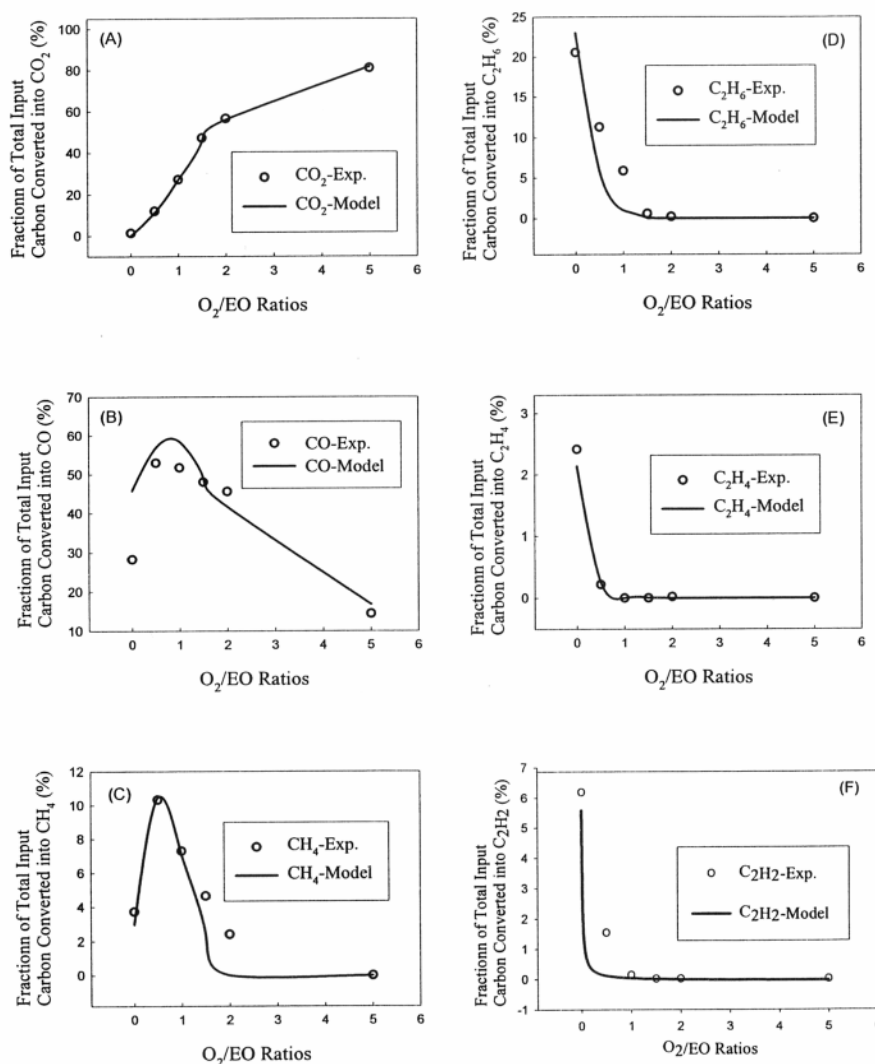


Figure 2. Comparison of modeling data with experimental data on the product concentrations at various O₂/EO ratios (input power = 30 W; operational pressure = 20 torr; Eo feeding concentration = 2%; total gas flow rate = 100 sccm).

FIVE MOST IMPORTANT REACTIONS RELATED TO C₂H₄O IN THE EO/O₂/AR PLASMA SYSTEM

Table 4 presents results from sensitivity analysis on the model for the relative importance of C₂H₄O decomposition reactions in the EO/O₂/Ar plasma system. Although the equation, H+O₂+M=HO₂+M, seems not to have much relation with the decomposition of EO, it is the most important decomposition reaction of EO over the operation regime. The reason for this is that the reactions H+O₂+M=HO₂+M first produce more HO₂ radicals, then HO₂ proceeds with the reaction HO₂+H = OH+OH further to form more OH radicals; finally, OH radicals participate in the reaction, C₂H₄O+OH=C₂H₃O+H₂O, to decompose more C₂H₄O. To conclude, the reaction H+O₂+M=HO₂+M enhances the decomposition reaction of EO via the following mechanisms.



THE REACTION PATHWAYS IN THE EO/AR AND EO/O₂/AR PLASMA SYSTEM

By summarizing the sequence of formation and dissipation reactions of the major species measured in the plasma reactor, we built up two reaction pathways, one for the EO/Ar plasma system and the other for the EO/O₂/Ar (O₂/EO=5.0) plasma system. They are shown in Figure 3 and Figure 4, respectively.

As seen in Figure 3, when no O₂ is added, the major decomposing route for EO, C₂H₄O+e⁻=CH₃CHO+e⁻, produces the intermediate, CH₃CHO. Then, CH₃CHO dissipates through two major routes, one makes it form CH₃ and CHO radicals, and the other leads to the formation of the other intermediate, CH₃CO. Furthermore, the CH₃ radical goes around a reaction loop to form a significant amount of C₂H₆ and a perceivable amount of C₂H₄ and C₂H₂, or terminates with radical H to form a small amount of CH₄.

As seen in Figure 4, when a large amount of O₂ is added, the major decomposing route for EO shifts to the reactions C₂H₄O+H=C₂H₃O+H₂ and C₂H₄O+OH=C₂H₃O+H₂O. Then, C₂H₃O dissipates to form the stable products, CO₂ and H₂O. Furthermore, because of the loop reaction for CH₃ to form C₂H₆ has been stopped. So, instead of forming C₂H₆, CH₃ forms the intermediate CH₂O; then it reacts further to form the final product CO₂.

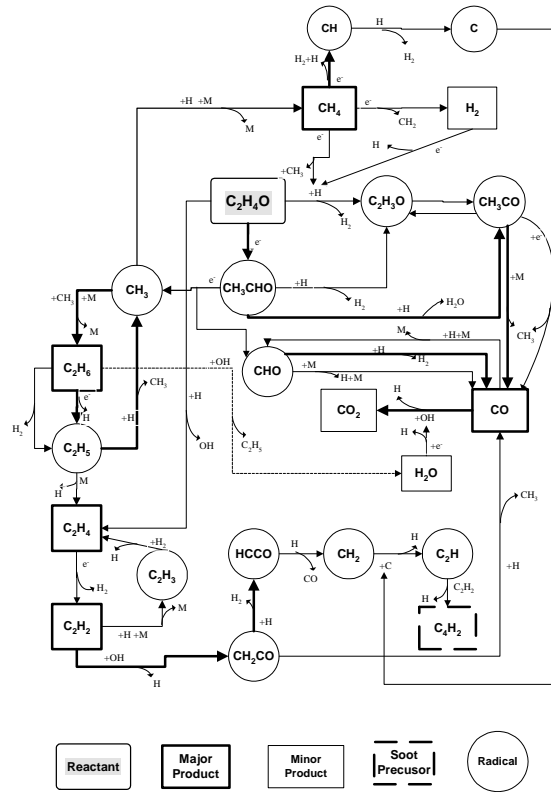


Figure 3. The reaction pathways of EO/ Ar plasma system.

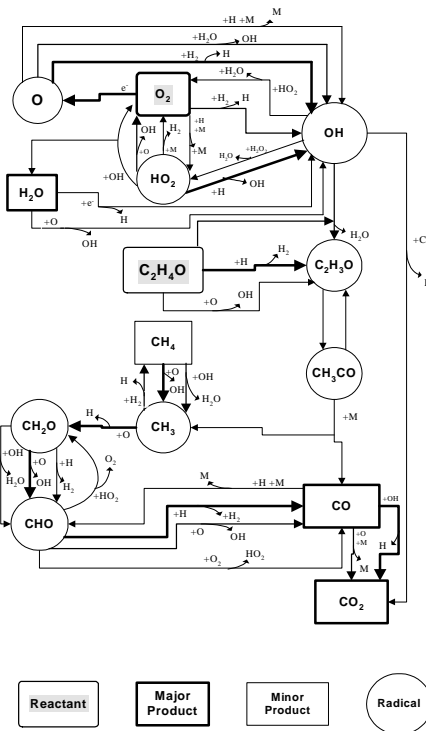


Figure 4. The reaction pathways of EO/O₂/Ar (O₂/EO=5.0) plasma system.

CONCLUSIONS

Results showed that the calculated decomposition fraction of EO and concentrations of products agree very well with the experiment's data. In addition, the decomposition reactions for EO were changing with varying O₂/EO ratios in the complex plasma system. The most important reaction with an O₂/EO ratio of zero was the electron dissociation reaction of EO, $C_2H_4O + e^- \rightarrow CH_3CHO + e^-$. However the most significant reaction with an O₂/EO ratio of 5.0 was the formation reaction of HO₂, which forms OH radicals further, then enhances the decomposition of C₂H₄O by the reaction, $C_2H_4O + OH = C_2H_3O + H_2O$.

The detail reaction pathways for decomposition of EO at various O₂/EO ratios in the RF plasma reactor tell us that the CH₃ radical goes around a reaction loop to form significant amount of C₂H₆ at zero of O₂/EO. And the loop reaction for CH₃ to form C₂H₆ has been stopped at 5.0 of O₂/EO, and instead of forming C₂H₆, CH₃ forms the intermediate CH₂O, then it reacts further to become the final product CO₂.

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