



Decomposition of Methyl Tert-Butyl Ether by Adding Hydrogen in a Cold Plasma Reactor

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ABSTRACT

Methyl tert-butyl ether (MTBE) is extensively used as an oxygenate and octane enhancer in gasoline. Its release to the environment has generated great public and governmental concern. In this study, we give a brief review of the decomposition of air toxics by the application of radio frequency (RF) plasma reactors and then present our study on decomposition of methyl tert-butyl ether by adding hydrogen in a cold plasma reactor. Based on our references, there are four types of the application in the RF plasma reactors are discussed, including: (i) **Application I.**: Converting methane, decomposing carbon dioxide, ethoxyethane, and ethylene oxide; (ii) **Application II.**: Decomposing methyl chloride, 1,1-C₂H₂Cl₂, and CH₂Cl₂; (iii) **Application III.**: Decomposing dichlorodifluoromethane, CHF₃, CH₂F₂, CCl₂F₂, and BF₃; (iv) **Application IV.**: Decomposing dichlorodifluoromethane, CH₃SH, CS₂, SF₆, and SF₆ + H₂S mixture. Moreover, this study demonstrates the feasibility of applying a radio frequency (RF) plasma reactor for decomposing and converting MTBE. Experimental results indicate that the decomposition efficiency (η_{MTBE}) and the fraction of total input carbon converted into CH₄, C₂H₂ and C₂H₄ ($F_{\text{CH}_4+\text{C}_2\text{H}_2+\text{C}_2\text{H}_4}$) increased with the input power and decreased as both the H₂/MTBE ratio and the MTBE influent concentration in the MTBE/H₂/Ar plasma environment increased. Interestingly, applying radio frequency plasma to the decomposition of MTBE while adding hydrogen constitutes alternative method of decomposing and converting MTBE into CH₄, C₂H₄, C₂H₂, iso-butane and iso-butene.

Keywords: Methyl tert-butyl ether (MTBE); Radio-frequency (RF); Plasma; Decomposition; Reaction.

INTRODUCTION AND A BRIEF REVIEW OF DECOMPOSITION OF AIR TOXICS IN RF PLASMA SYSTEM

Traffic-related pollutants have received a great deal of interest due to their inherent toxicities and possible heterogeneous reactions with other components in the atmosphere (Saunders *et al.*, 1997; Cheng *et al.*, 2010; Chuang *et al.*, 2010a, b; Shen *et al.*, 2010; Han *et al.*, 2011; Ma *et al.*, 2011). Cheng *et al.* (2010) investigated the gas/particle partitioning of dioxins in exhaust gases from automobiles. In their study, 6 sport utility vehicles (SUVs), 6 diesel passenger vehicles (DPVs), and 3 heavy duty diesel vehicle (HDDV) were examined using chassis dynamometer

tests for measuring vehicular dioxin emissions. They indicated the mean PCDD/F I-TEQ emission factors were 0.101, 0.0688 and 0.912 ng I-TEQ/km for the SUVs, DPVs and HDDV, respectively. Moreover, high concentrations of benzo(a)pyrene (BaP) and benzo(a)pyrene-equivalent carcinogenic power (BaPE) demonstrated the potential health risk of traffic-related PAHs at the roadside area in Xi'an. The ratio of between indeno(1,2,3-*cd*)pyrene (IP) and benzo(g,h,i)perylene (BghiP) is also used to test the primary source of PAHs. The ratio of IP/(IP + BghiP) and IP/BghiP indicated that the primary source of PAHs was gasoline vehicles at this roadside area (Shen *et al.*, 2010).

Methyl *tert*-butyl ether (MTBE), an oxygenate, has become a common ingredient in gasoline, because of its excellent octane rating and positive contribution to air quality in large cities (U.S. EPA, 1988; 1993; Davidson and Creek, 2000). MTBE has been successfully added to gasoline to meet increasingly tough laws on liquid fuels. The positive effects of MTBE include a reduction in

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particulate emissions, unburnt hydrocarbons, CO and exhaust emissions. However, both the pollution of the environment by MTBE and the possible adverse effects of exposure to MTBE are of public concern (Johanson *et al.*, 1995; Lacy *et al.*, 1995; Brown, 1997; Lillquist and Zeigle, 1998; Nihlen *et al.*, 1998; Hong *et al.*, 1999; Deeb *et al.*, 2001).

Johanson *et al.* (1995) measured the blood, water, and olive oil/air partition coefficients in vitro of MTBE, ETBE, TAME and tertiary butyl alcohol (TBA), a metabolite of MTBE and ETBE. Moreover, Johanson *et al.* (1995) exposed 10 healthy male volunteers to MTBE vapor at 5, 25 and 50 ppm for 2 h during light physical exercise. Their results show that the concentration of MTBE and TBA in blood was proportional to exposure level suggesting linear kinetics up to 50 ppm. The half life of 7–10 h in blood and urine indicates that TBA would be more suitable than the parent compound as a biomarker for MTBE exposure (Johanson *et al.*, 1995). Additionally, MTBE was banned as a gasoline additive in California in 2003 and New York is likely to act similarly (Governor, 2003). Potential technologies for decomposing or removing MTBE have attracted much interest globally the world (Trotta and Miracca, 1997; Fields *et al.*, 1998; Anderson, 2000; Chambreau *et al.*, 2000). Plasma technology is preferred over biodegradation, which is time-consuming, for decomposing MTBE.

RF plasma is a branch of nonequilibrium plasma. Since both electrons and some activated ions therein have more kinetic energy than typical molecules, RF plasma is also called cold plasma (Eliasson and Kogelschatz, 1991). An advantage of using the RF plasma reactor is that a conventional reaction therein can be completed at a lower temperature elsewhere (Hsieh *et al.*, 1998a). Many studies have demonstrated that the destruction or treatment of hazardous gases by applying RF plasma technology is very practical (Lee *et al.*, 1996; Li *et al.*, 1996; Hsieh *et al.*, 1998a, b, c; Wang *et al.*, 1999a, b; Liao *et al.*, 2000; Wang *et al.*, 2000; Hsieh *et al.*, 2001; Liao *et al.*, 2001; Tsai *et al.*, 2001; Shih *et al.*, 2002; Tsai *et al.*, 2002; Shih *et al.*, 2003; Tsai *et al.*, 2003; Wang *et al.*, 2003; Tsai *et al.*, 2004; Liao *et al.*, 2005; Wang *et al.*, 2005a, b; Hsieh *et al.*, 2007; Tsai *et al.*, 2007). The above mentioned cited articles (from 1996 to 2007) show that RF power is delivered through the power meter and the matching unit to an outer copper electrode that is wrapped around the reactor, the other electrode is earthed. The above mentioned system is generally inductively coupled type. It means that, in such system, the external electrode and the glass reactor wall beneath it, together with the conductive plasma inside the reactor, generated a capacitor that enabled capacitive coupling of RF power into the discharge. In order to insight the RF plasma technology, a brief review of the decomposition of air toxics by the application of radio frequency plasma reactors is presented as follows. Based on our references, there are four types of the application in the RF plasma reactors can be discussed, including: (i) **Application I.**: Converting methane, decomposing carbon dioxide, ethoxyethane, and ethylene oxide; (ii) **Application**

II.: Decomposing methyl chloride, 1,1-C₂H₂Cl₂, and CH₂Cl₂; (iii) **Application III.**: Decomposing dichlorodifluoromethane, CHF₃, CH₂F₂, CCl₂F₂, and BF₃; (iv) **Application IV.**: Decomposing dichlorodifluoromethane, CH₃SH, CS₂, SF₆, and SF₆ + H₂S mixture.

Application I. Converting Methane, Decomposing Carbon Dioxide, Ethoxyethane, and Ethylene Oxide

Application of radio-frequency (RF) plasma as an alternative technology for converting methane or decomposing carbon dioxide, ethoxyethane, and ethylene oxide are demonstrated. Several research articles are discussed as follows:

(1) Converting Methane by Using an RF Plasma Reactor

Hsieh *et al.* (1998a) reported a radio-frequency (RF) plasma system was used to convert methane gas. The reactants and final products were analyzed by using an FTIR (Fourier transform infrared spectrometer). The effects of plasma operational parameters, including feeding concentration (C) of CH₄, operational pressure (P) in the RF plasma reactor, total gas flow rate (Q) and input power wattage (W) for CH₄ decomposition were evaluated. The results showed that the CH₄ decomposition fraction increases with increasing power input, decreasing operational pressure in the RF plasma reactor, decreasing CH₄ feeding concentration, and decreasing total gas flow rate (Hsieh *et al.*, 1998a).

(2) Decomposition of Carbon Dioxide in the RF Plasma Environment

Application of radio-frequency (RF) plasma as an alternative technology for the decomposition of carbon dioxide with methane gas is demonstrated (Hsieh *et al.*, 1998c). The results revealed that in CO₂/CH₄/Ar plasma, the best decomposition fraction of carbon dioxide was 60.0%, which occurs around 316°C in the condition designed for 5% feeding concentration of CO₂, 5% feeding concentration of CH₄, 20 torr operation pressure, 100 sccm total gas flow rate and 90 watts input power wattage. The CH, CH₂ and CH₃ radicals obtained from the destruction of CH₄ could result effectively in high decomposition of CO₂ in the plasma reactor (Hsieh *et al.*, 1998c). Hsieh *et al.* (1998c) show the optimal mathematical models based on the experimental data obtained and tested the proposal model by means of sensitivity analysis, which shows that the input power wattage (W) was the most sensitive parameter for the CO₂ decomposition.

(3) Decomposition of Ethoxyethane in the Cold Plasma Environment

For ethoxyethane (EOE) contained gas, a radio frequency (RF) plasma system was also used to decompose the EOE contained gas (Liao *et al.*, 2000). The reactants and final products were analyzed by using an FTIR (Fourier Transform Infrared) spectrometer. The effects of plasma operational parameters, including input power wattage (W), equivalence ratios (Φ), feeding concentration (C) of EOE and total gas flow rate (Q) for EOE decomposition were

also evaluated. Liao *et al.* (2000) gave the possible reaction pathways for EOE decomposition and the formation of final products in the study. They suggest that at lower input power wattages, the creation of glow discharge is strongly dependent on the plasma production index (PPI). In their study, when input power wattages are smaller than 30 W, the minimum values of PPI to create glow discharge ranged between 18.2 and 19.0. Their result demonstrates that the decomposition fraction of EOE could reach 100% under most operational conditions in the RF plasma reactor (Liao *et al.*, 2000).

(4) Decomposition of Ethylene Oxide in the RF Plasma Environment

For ethylene oxide (EO) contained gas, a radio frequency (RF) plasma system was also used to decompose the ethylene oxide (EO) contained gas in the EO/Ar, and EO/O₂/Ar system, respectively. In the RF plasma system, due to the importance of the high-energy electrons, the EO decomposition fraction in plasma reaction increased with decreasing operational pressure, while that of thermal reaction, reported by previous investigations, increased with increasing operational pressure (Liao *et al.*, 2001). However, owing to the electrophilic characteristic of oxygen atoms in the EO molecule causing the effect of electron attachment, in conditions of higher EO feeding concentration, the pressure dependence became the same for both plasma- and thermal-reaction (Liao *et al.*, 2001). The EO oxidation reaction has also been investigated; the result shows that EO almost completely oxidized at 600–692 K gas temperature. The main products for the EO/Ar system are CO, CH₄, C₂H₆, C₂H₄, and C₂H₂, and those for the EO/O₂/Ar system are CO₂ and H₂O (Liao *et al.*, 2001).

Liao *et al.* (2005) report 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 (Liao *et al.*, 2005). They concluded some crucial points and we cited those important statements as follows.

- “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, C₂H₄O + e⁻ → CH₃CHO + 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, C₂H₄O + OH = C₂H₃O + H₂O” (Liao *et al.*, 2005).
- “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” (Liao *et al.*, 2005).

Application II. Decomposing Methyl Chloride, 1,1-C₂H₂Cl₂, and CH₂Cl₂

Application of radio-frequency (RF) plasma as an alternative technology for the decomposition of methyl chloride, 1,1-C₂H₂Cl₂ contained gas, and CH₂Cl₂ is also demonstrated. Several research articles are discussed as follows.

(1) Decomposition of Methyl Chloride in the RF Plasma Environment

Application of radio-frequency (RF) plasma as an alternative technology for the decomposition of methyl chloride (CH₃Cl) with oxygen is demonstrated by Hsieh *et al.* (1998b). Hsieh *et al.* (1998b) concluded that in the CH₃Cl/O₂/Ar plasma, the decomposition fraction of CH₃Cl was over 99.99%, which occurred around 440°C in the condition designed for 3% of CH₃Cl feeding concentration, 1.0 of equivalence ratio (φ), 20 Torr of operation pressure, 100 sccm of total gas flow rate and 100 watts of input power wattage. They indicated that the CH₃Cl decomposition fractions increase when the equivalence ratio is raised to values around or below stoichiometry; and then decrease either sharply (50 W) or moderately (70 W) when the equivalence ratio goes up or down to values exceeding stoichiometry (Hsieh *et al.*, 1998b). However, there is no significant difference for those in higher input power wattages (both 90 and 100 W). Moreover, at higher φ values, higher CH₃Cl feeding concentrations, and higher input power wattages, more soot formation and polymerization were also found in the plasma reactor. These resulted in a lower carbon balance in the effluent gas stream (Hsieh *et al.*, 1998b). Both methyl chloride decomposition efficiency and fraction of total-carbon input converted into CO and CO₂ were decreased by increasing the methyl chloride feeding concentration. Besides, input power wattage (W) is the most important parameter in governing the temperature in the plasma reactor because the plasma reaction is associated mainly with the energy provided (Hsieh *et al.*, 1998b). Their study indicates the significance of sensitivity for the T (°C) in the plasma reactor is: W > C_{CH₃Cl} > φ.

(2) Decomposition of 1,1-C₂H₂Cl₂ Contained Gas in an RF Plasma Reactor

Lee *et al.* (1996) studied phosgene formation from the decomposition of 1,1-C₂H₂Cl₂ contained gas in an RF plasma reactor. The RF plasma system was used to decompose the 1,1-dichloroethylene (DCE) contained gas. The reactants and final products were analyzed by using an FTIR (Fourier Transform Infrared Spectroscopy). The possible reaction pathways for DCE decomposition and phosgene (COCl₂) formation were built up and discussed. Lee *et al.* (1996) revealed both DCE decomposition efficiency and the fraction of total carbon mass converted into CO₂ and CO were decreased by the increasing DCE feeding concentration. The DCE decomposition efficiency at varied equivalence ratios, φ (stoichiometric O₂/actual O₂), was controlled by both oxidation and energy transfer efficiency. They also found at lower equivalence ratios

having an excess of oxygen, a larger amount of COCl_2 was formed due to a higher oxygen-feeding concentration. Moreover, higher input power wattage can increase both the DCE decomposition efficiency and the fraction of total-carbon mass converted into CO_2 and CO , resulting in the reduction of the COCl_2 effluent concentration (Lee et al., 1996).

(3) Decomposition of CH_2Cl_2 in the RF Plasma Environment

In the investigation by Li et al. (1996), a RF plasma system was also applied to decompose a dichloromethane (CH_2Cl_2) containing gas. Analyses of the reactants and final products were conducted by using Fourier Transform Infrared Spectroscopy. Moreover, the effects of plasma operation-parameters, including the gas flow rate, the feeding CH_2Cl_2 concentration, the equivalence ratio ϕ (= stoichiometric O_2 needed/actual O_2 used) and the input power wattage, for CH_2Cl_2 decomposition and for the fraction of total carbon input converted into CO_2 and CO were investigated (Li et al., 1996). Mole fraction profiles for each experimental condition were determined for the reactants (CH_2Cl_2 and O_2) and for CO , CO_2 , H_2O , HCl , CHCl_3 , CCl_4 , COCl_2 , C_2HCl_3 and C_2Cl_4 (Li et al., 1996).

Application III. Decomposing Dichlorodifluoromethane, CHF_3 , CH_2F_2 , CCl_2F_2 , and BF_3

Application of radio-frequency plasma as an alternative technology for the decomposition of dichlorodifluoromethane by adding hydrogen is also demonstrated. Moreover, the reaction mechanisms in both a $\text{CHF}_3/\text{O}_2/\text{Ar}$ and $\text{CHF}_3/\text{H}_2/\text{Ar}$ RF plasma environment or in Both $\text{CCl}_2\text{F}_2/\text{O}_2/\text{Ar}$ and $\text{CCl}_2\text{F}_2/\text{H}_2/\text{Ar}$ RF Plasma Environment are investigated insightfully. Several research articles are discussed as follows.

(1) Decomposition of Dichlorodifluoromethane by Adding Hydrogen in a Cold Plasma System

For the destruction of chlorofluorocarbons (CFCs), it has drawn great attention because of its well-known depletion of the ozone layer at the stratosphere. In 1999, Wang et al. (1999a) studied the application of RF plasma for the decomposition and conversion of dichlorodifluoromethane (CFC-12 or CCl_2F_2). Wang et al. (1999a) mentioned that the decomposition efficiency ($\eta_{\text{CFC-12}}$) and the fraction of total carbon input converted into CH_4 and C_2H_2 ($F_{\text{CH}_4+\text{C}_2\text{H}_2}$) in H_2 and Ar mixtures have been investigated as a function of input power wattage, $\text{H}_2/\text{CFC-12}$ ratio, operational pressure, and CFC-12 feeding concentration by using response surface methodology and model sensitivity analysis (Wang et al., 1999a). Their results revealed that the $\eta_{\text{CFC-12}}$ is over 94% and the $F_{\text{CH}_4+\text{C}_2\text{H}_2}$ is over 80% under the condition of 100 W of input power wattage, 7.0 of $\text{H}_2/\text{CFC-12}$ ratio, 15 Torr of operational pressure, and 7.6% of CFC-12 feeding concentration (Wang et al., 1999a). They also use the method of sensitivity analysis to test the $\eta_{\text{CFC-12}}$ and $F_{\text{CH}_4+\text{C}_2\text{H}_2}$. It is indicated both the $\eta_{\text{CFC-12}}$ and $F_{\text{CH}_4+\text{C}_2\text{H}_2}$ are more sensitive to CFC-12 feeding concentration and input power wattage. From this study,

we understand CFC-12 could be converted into CH_4 and C_2H_2 up to 80% of conversion in a hydrogen-based RF plasma system.

(2) Reaction Mechanisms in both a $\text{CHF}_3/\text{O}_2/\text{Ar}$ and $\text{CHF}_3/\text{H}_2/\text{Ar}$ RF Plasma Environment

Wang et al. (1999b) studied the decomposition of trifluoromethane (CHF_3 or HFC-23) in a RF plasma system. Wang et al. (1999b) obtained some important results and we cited them originally as follows.

- “The CHF_3 decomposition fractions (η_{CHF_3}) and mole fractions of detected products in the effluent gas streams of $\text{CHF}_3/\text{O}_2/\text{Ar}$ and $\text{CHF}_3/\text{H}_2/\text{Ar}$ plasma systems, respectively, have been determined. The effects of four experimental parameters, input power, O_2/CHF_3 or H_2/CHF_3 ratio, operational pressure, and the CHF_3 feeding concentration were investigated” (Wang et al., 1999b)
- “The same species detected in the effluent gas streams of both $\text{CHF}_3/\text{O}_2/\text{Ar}$ and $\text{CHF}_3/\text{H}_2/\text{Ar}$ plasma systems were CH_2F_2 , CF_4 , HF , and SiF_4 . However, the CO_2 and COF_2 were detected only in the $\text{CHF}_3/\text{O}_2/\text{Ar}$ plasma system and the CH_4 , C_2H_2 , and CH_3F were detected only in the $\text{CHF}_3/\text{H}_2/\text{Ar}$ plasma system” (Wang et al., 1999b).
- “The results of a model sensitivity analysis showed that the input power was the most influential parameter for η_{CHF_3} both in the $\text{CHF}_3/\text{O}_2/\text{Ar}$ and $\text{CHF}_3/\text{H}_2/\text{Ar}$ plasma systems” (Wang et al., 1999b).
- “The addition of hydrogen for CHF_3 decomposition can produce a significant amount of HF and the main carbonaceous byproducts were CH_4 and C_2H_2 . Even though the η_{CHF_3} in the $\text{CHF}_3/\text{H}_2/\text{Ar}$ plasma system is lower than that in the $\text{CHF}_3/\text{O}_2/\text{Ar}$ plasma system, but due to the more advantages mentioned above, a hydrogen-based RF plasma system is a better alternative to decompose CHF_3 ” (Wang et al., 1999b).

(3) Reaction Mechanism in both $\text{CCl}_2\text{F}_2/\text{O}_2/\text{Ar}$ and $\text{CCl}_2\text{F}_2/\text{H}_2/\text{Ar}$ RF Plasma Environment

In 2000, Wang et al. (2000) presented the decomposition of dichlorodifluoromethane (CCl_2F_2 or CFC-12) in a radio frequency (RF) plasma system. Here lists their major observations and cited them originally as follows.

- “The CCl_2F_2 decomposition fractions and mole fractions of detected products in the effluent gas stream of $\text{CCl}_2\text{F}_2/\text{O}_2/\text{Ar}$ and $\text{CCl}_2\text{F}_2/\text{H}_2/\text{Ar}$ plasma, respectively, have been determined. The experimental parameters including input power wattage, $\text{O}_2/\text{CCl}_2\text{F}_2$ or $\text{H}_2/\text{CCl}_2\text{F}_2$ ratio, operational pressure, and CCl_2F_2 feeding concentration were investigated” (Wang et al., 2000).
- “The main carbonaceous product in the $\text{CCl}_2\text{F}_2/\text{O}_2/\text{Ar}$ plasma system was CO_2 , while that in the $\text{CCl}_2\text{F}_2/\text{H}_2/\text{Ar}$ plasma system was CH_4 and C_2H_2 ” (Wang et al., 2000).
- “The results of the experiments showed that the highly electronegative chlorine and fluorine would

easily separate from the CCl_2F_2 molecule and combine with the added reaction gas. This led to the reactions terminated with the CO_2 , CH_4 , and C_2H_2 formation, because of their high bonding strength. The addition of hydrogen would form a preferential pathway for the HCl and HF formations, which were thermodynamically stable diatomic species that would limit the production of CCl_3F , CClF_3 , CF_4 , and CCl_4 " (Wang et al., 2000).

- "The HCl and HF could be removed by neutral or scrubber method. Hence, a hydrogen-based RF plasma system provided a better alternative to decompose CCl_2F_2 " (Wang et al., 2000).

(4) Decomposition of Boron Trifluoride in the RF Plasma Environment

In 2003, a radio frequency (RF) plasma system used to decompose boron trifluoride (BF_3) was also examined (Wang et al., 2003). The BF_3 decomposition fractions (η_{BF_3}) were determined in effluent gas streams of $\text{BF}_3/\text{CH}_4/\text{Ar}$, $\text{BF}_3/\text{O}_2/\text{Ar}$ and $\text{BF}_3/\text{O}_2(\text{glass})/\text{Ar}$ plasma systems. The η_{BF_3} in the $\text{BF}_3/\text{CH}_4/\text{Ar}$ plasma system was 49.8%, higher than that in the $\text{BF}_3/\text{O}_2/\text{Ar}$ and $\text{BF}_3/\text{O}_2(\text{glass})/\text{Ar}$ plasma system. The reaction in the $\text{BF}_3/\text{O}_2/\text{Ar}$ plasma system generated B_2O_3 fine particles and led to the deposition of a white substance on the surface of the reactor. The η_{BF_3} was only around 25% for mixing with O_2 , even when the input power exceeded 120 Watts, but the generation of fine particles in the system warrants much more investigation (Wang et al., 2003).

Application IV. Decomposing Dichlorodifluoromethane, CH_3SH , CS_2 , SF_6 , and $\text{SF}_6 + \text{H}_2\text{S}$ Mixture

Application of radio-frequency plasma as an alternative technology for the decomposition of CH_3SH , CS_2 , and SF_6 is also demonstrated. Moreover, the Difference in conversions between dimethyl sulfide and methanethiol in a cold plasma environment are also investigated. Several research articles are discussed as follows.

(1) Decomposition of CH_3SH in a RF Plasma Reactor: Reaction Products and Mechanisms

Tsai et al. (2001) studied the application of the RF cold plasma method to the decomposition of methanethiol (methyl mercaptan, CH_3SH) at different $\text{O}_2/\text{CH}_3\text{SH}$ ratios (0–4.5), with various input powers (20–90 W), and at constant operating pressure (30 Torr). The species detected in the $\text{CH}_3\text{SH}/\text{O}_2/\text{Ar}$ RF plasma were SO_2 , CS_2 , OCS , CO , CO_2 , CH_4 , C_2H_4 , C_2H_2 , H_2 , H_2O , HCOH , and CH_3OH . However, CS_2 , CH_4 , C_2H_4 , C_2H_2 , H_2 , H_2S , CH_3SCH_3 (DMS), and $\text{CH}_3\text{S}_2\text{CH}_3$ (DMDS) were detected in the $\text{CH}_3\text{SH}/\text{Ar}$ RF plasma (Tsai et al., 2001). Here lists their major observations and cited them originally as follows.

- In the $\text{CH}_3\text{SH}/\text{Ar}$ plasma, over 83.7% of the total sulfur input was converted into CS_2 at 60 W; this is due to the lack of competition between O and S and the thermodynamic stability of CS_2 . (Tsai et al., 2001)
- In the oxygen-rich conditions of the $\text{CH}_3\text{SH}/\text{O}_2/\text{Ar}$ plasma, the most predominant sulfur-containing

compound was SO_2 . (Tsai et al., 2001)

- As the feed $\text{O}_2/\text{CH}_3\text{SH}$ ratio was increased, MSO_2 was increased, while MCS_2 was decreased simultaneously. MOCS was reduced by increasing either the $\text{O}_2/\text{CH}_3\text{SH}$ ratio or the applied power. (Tsai et al., 2001)
- From the decay of CS_2 and the generation of CO at a lower $\text{O}_2/\text{CH}_3\text{SH}$ ratio of 0.6, CS , CS_2 , and CO were suggested as the primary species to react with O, OH, O_2 , S, or S_2 and then to form OCS . (Tsai et al., 2001)

(2) Formation of Solid Sulfur by Decomposition of CS_2 in Plasma Environment

The conventional thermal processes for treating toxic carbon disulfide (CS_2) gas were by the oxidation of sulfur on CS_2 to form SO_2 . Interestingly, in 2002, Tsai et al. (2002) reported that using a radio-frequency cold plasma reactor in the oxygen-lean condition ($\text{O}_2/\text{CS}_2 = R = 0.6$) at the applied power of 90 W, the decomposition fraction of CS_2 could reach 88.2%, and there was 76.9% of input sulfur mass from CS_2 converted into solid sulfur with the purity of 99.2% (Tsai et al., 2002). In this study, no solid sulfur was observed for the no-oxygen ($R = 0$) or oxygen-rich conditions ($R = 3.0$). Such results provided an approach for sulfur recovery to reduce the emissions of both CS_2 and SO_2 (Tsai et al., 2002).

(3) Decomposition of SF_6 in an Plasma Environment

In general, sulfur hexafluoride (SF_6) contained gas is a common pollutant emitted during the etching process used in the semiconductor industry. Shih et al. (2002) studied the application of RF plasma in the decomposition of SF_6 . The decomposition fraction of SF_6 and the mole fraction profile of the products were investigated as functions of input power and feed O_2/SF_6 ratio in a RF plasma reactor. Their results revealed that at 40 W, SF_6 exceeded 99%, and the reaction products were almost all converted into stable compounds such as SiF_4 , SO_2 , and F_2 with or without the addition of oxygen (Shih et al., 2002). The results of this work can be used to design a plasma/chemical system for online use in a series of a manufacturing process to treat SF_6 containing exhaust gases (Shih et al., 2002).

(4) Decomposition of SF_6 and H_2S Mixture in Radio Frequency Plasma Environment

Sulfur hexafluoride (SF_6) is a gaseous pollutant generated in manufacturing processes in the semiconductor industry. Shih et al. (2003) have applied the hydrogen sulfide (H_2S), as a reductant, to treat SF_6 in a radio frequency (RF) plasma system. Shih et al. (2003) mentioned that SiF_4 and SO_2 were the two dominant species detected in the glass reactor in the SF_6/Ar plasma system; other detected species were SO_2F_2 , SOF_2 , and SOF_4 . In the $\text{SF}_6/\text{H}_2\text{S}/\text{Ar}$ plasma system, HF and elemental sulfur were the main produced species (Shih et al., 2003). Shih et al. (2003) also indicated that although the species SiF_4 , SO_2 , SO_2F_2 , SOF_2 , and SOF_4 were detected in the $\text{SF}_6/\text{H}_2\text{S}/\text{Ar}$ plasma system, adding H_2S clearly inhibited the generation of these

byproducts of SiO₂ etching. They also stated that at an input power of 5 W and an H₂S/SF₆ ratio of 2.9, the mass fraction of fluorine from feed SF₆ converted into HF was 95.3%, while the mass fraction of sulfur from feed SF₆ and H₂S converted into elemental sulfur was 96.1% (Shih et al., 2003).

(5) Conversion of SO₂ into Elemental Sulfur by Using the RF Plasma Technique

In 2004, Tsai et al. (2004) demonstrated a new approach for converting SO₂ into elemental sulfur by adding CH₄ in a RF plasma reactor. With the applied power (P) of the RF reactor specified at 90 W and operating pressure set at 4000 N/m², Tsai et al. (2004) demonstrated that as the CH₄/SO₂ ratio (R) was increased from 0.3 to 1.0, most sulfur-containing products were in the form of elemental sulfur (Tsai et al., 2004). In fact, their results indicate that the use of the RF plasma technique was not only beneficial to convert SO₂, but also was able to convert CH₄ into useful materials. Here lists their key observations and cited them originally as follows.

- “While R was increased from 1 to 2, the content of elemental sulfur was decreased significantly, but CS₂ was increased dramatically. While R was increased from 2 to 3, both elemental sulfur and CS₂ contents became quite comparable. Nevertheless, it was found that both H₂ and CO (that is, syngas) were the main nonsulfur-containing products under all testing conditions” (Tsai et al., 2004).
- “For R = 0 (that is, no CH₄ was introduced), it was found that the SO₂ conversion (i.e., η_{SO_2}) = 0.084, indicating that the RF plasma process was inadequate to convert pure SO₂ without adding CH₄ as a reducing agent” (Tsai et al., 2004).
- “While R was increased to 2, it was found that η was improved significantly to 0.968 accompanied with η_{CH_4} = 0.999. But as R was increased from 2 to 3, both η_{SO_2} and η_{CH_4} were slightly decreased. Both η_{SO_2} and η_{CH_4} also were sensitive to the applied power (P). As P was increased from 15 W to 90 W at R = 2, it was found that both η_{SO_2} and η_{CH_4} were increased dramatically from 0.247 and 0.320 to 0.968 and 0.999, respectively. But as P was increased from 90 W to 120 W, the increase on both η_{SO_2} and η_{CH_4} became very limited” (Tsai et al., 2004).

Finally, Tsai et al. (2004) suggests that the operating condition of R = 2 and P = 90 W would be the most appropriate combination for SO₂ conversion.

(6) Conversion of Carbonyl Sulfide Using a Low-Temperature Discharge Approach

Tsai et al. (2007) demonstrated a low-temperature radio-frequency (RF) plasma approach was used to destruct COS for removing sulfur. In general, carbonyl sulfide (COS) are usually yielded from the petrification industry or steel-making plants. In this study, high concentration of COS was successfully destructed and converted into other sulfur-containing products by adding H₂ or O₂, or without an additive, utilizing a low-pressure RF discharge

approach. Tsai et al. (2007) show that no H₂S was detected, which is very different from the traditional catalytic removal process, including COS hydrogenation (COS + 4H₂ = H₂S + CH₄ + H₂O) and hydrolysis of COS and CS₂ (COS + H₂O → H₂S + CO₂) (Tsai et al., 2007). Tsai et al. (2007) indicated that the discharge approach replaced major product H₂S with elemental sulfur that can be easily recovered with or without H₂, and can avoid the requirement of the sequential Claus reaction in order to convert H₂S into elemental sulfur. However, due to the relatively low pressure, this approach is not currently practical (Tsai et al., 2007).

(7) Difference in Conversions between Dimethyl Sulfide and Methanethiol in a Cold Plasma Environment

In 2003, Tsai et al. (2003) compared the conversion of two malodorous substances, dimethyl sulfide (CH₃SCH₃, DMS) and methanethiol (CH₃SH) in a cold plasma reactor. The DMS and CH₃SH were successfully destroyed at room temperature. Here lists their two major observations and cited them originally as follows.

- “DMS decomposed less than CH₃SH at the same conditions. In oxygen-free condition, CS₂ and hydrocarbons were the major products, while SO₂ and CO_x were main compounds in oxygen-rich environments” (Tsai et al., 2003).
- “The DMS/Ar plasma yielded more hydrocarbons and less CS₂ than that of CH₃SH/Ar plasma. In the CH₃SH/O₂/Ar plasma, rapid formation of SO and CO resulted in the yields much more amounts of SO₂ and CO₂ than those in the DMS/O₂/Ar plasma; and remained only a trace of total hydrocarbons, CH₂O, CH₃OH, CS₂, and OCS” (Tsai et al., 2003).

Recently, a treatment of cooking oil exhaust by plasma technology and a numerical investigation of corona plasma region are also reported. In 2007, Hsieh (2007) investigated the treatment of cooking oil exhaust by the application of combining atmospheric plasma technology and enzyme scrubbing. The results show the addition of NOE-7F in the enzyme scrubbing had the enhanced effect on the particle-bound water-soluble ions removal and mainly promoted highly the hydrophilicity of particle-bound water-soluble ions in the water scrubber. Thus, the application of combining atmospheric plasma technology and enzyme scrubbing has a high potential for practical application. In 2010, Kim et al. (2010) studied numerical investigation of corona plasma region in negative wire-to-duct corona discharge. In their article, a novel computation method calculating the plasma region thickness was presented with the plasma region model.

Based on the above-mentioned, we understand many RF plasma reactors can easily reach high decomposing or converting performance on the treatment of air toxics. Therefore, in this study, MTBE and H₂ mixtures were introduced into an RF plasma reactor with an operational pressure of 20 Torr. Three important operational parameters - input power, H₂/MTBE ratio and MTBE influent concentration - were considered. Additionally, the effect of operational conditions on the deposition was investigated.

This study aims to develop a feasible plasma technology for MTBE decomposition and the conversion of the carbon on MTBE into methane (CH_4), ethane (C_2H_6), acetylene (C_2H_2), *iso*-butene (*iso*- C_4H_8) and *iso*-butane (*iso*- C_4H_{10}). This work also aims to provide insights into the use of MTBE and oxygenate in gasoline to support both environmental treatment and environmental management decisions on the use of MTBE as a fuel additive.

MATERIALS AND METHODS

Fig. 1 schematically depicts the experimental apparatus used in this study, which has been detailed elsewhere (Hsieh *et al.*, 2001). The flows of all gases were maintained using a Tylan type 1179 mass flow controller at a total flow rate of 100 sccm. The gases were introduced into a mixing vessel. After it was completely mixed, MTBE/ H_2 /Ar gas was introduced into a 4.14 cm (inner diameter, I.D.) \times 15 cm (height) cylindrical glass reactor. A plasma generator (PFG 600 RF, Fritz Huttinger Elektronik GmbH) at 13.56 MHz, with a matching unit (Matchbox PFM), produced the RF plasma discharge. RF power was delivered through the power meter and a matching unit, onto two outer copper electrode sheets that surrounded the reactor. The spacing between the two electrode sheets was 5 mm to ensure constant RF power. The pressure of the system was reduced below 10^{-3} Torr using a diffusion pump before each experimental run to

eliminate contamination. The operating conditions were an operating pressure of 20 Torr, a total flow rate of 100 sccm, an H_2 /MTBE ratio from 1 to 10 and an applied power from 20 to 70W. Initially, both reactants and final products were identified by gas chromatography/mass spectrometry (HP 5890A PLUS GC/MS). Then, all species were identified and quantified using an on-line Fourier Transform Infrared (FT-IR) spectrometer (Bio-Rad Model FTS-7). The concentrations of vapor reactants and products were calibrated by withdrawing unreacted gases directly through the sampling tube linked to the FT-IR. The mass of the species was calculated by comparing the response factor (absorbance height/concentration) of standard gas to that of the species at a given IR wave number.

The FT-IR wave numbers of the absorbance-zone ranges of the 11 species considered in this study, were CO (1970–2230 $1/\text{cm}$), CO_2 (600–730, 2230–2400, 3500–3750 $1/\text{cm}$), CH_4 (1170–1400, 2825–3180 $1/\text{cm}$), C_2H_2 (300–850, 1200–1440, 3160–3370 $1/\text{cm}$), C_2H_4 (807–1162, 1400–1600, 2880–3285 $1/\text{cm}$), CH_3OH (900–1150, 1150–1720, 2800–3900 $1/\text{cm}$), *i*- C_4H_8 (840–1100, 2800–3200 $1/\text{cm}$), *i*- C_4H_{10} (1300–1550, 2840–3000 $1/\text{cm}$), HCHO (1680–1800, 2700–3000 $1/\text{cm}$), CH_3CHO (1000–1900, 2600–3100 $1/\text{cm}$), and MTBE (1000–1500, 2800–3100 $1/\text{cm}$). The FT-IR wave numbers of the centers of the absorbance peaks were CO (2169, 2117 $1/\text{cm}$), CO_2 (668, 2358, 3733, 3703, 3627, 3598 $1/\text{cm}$), CH_4 (1304, 3015, 3076, 3085 $1/\text{cm}$), C_2H_2 (730, 1305, 3268, 3285,

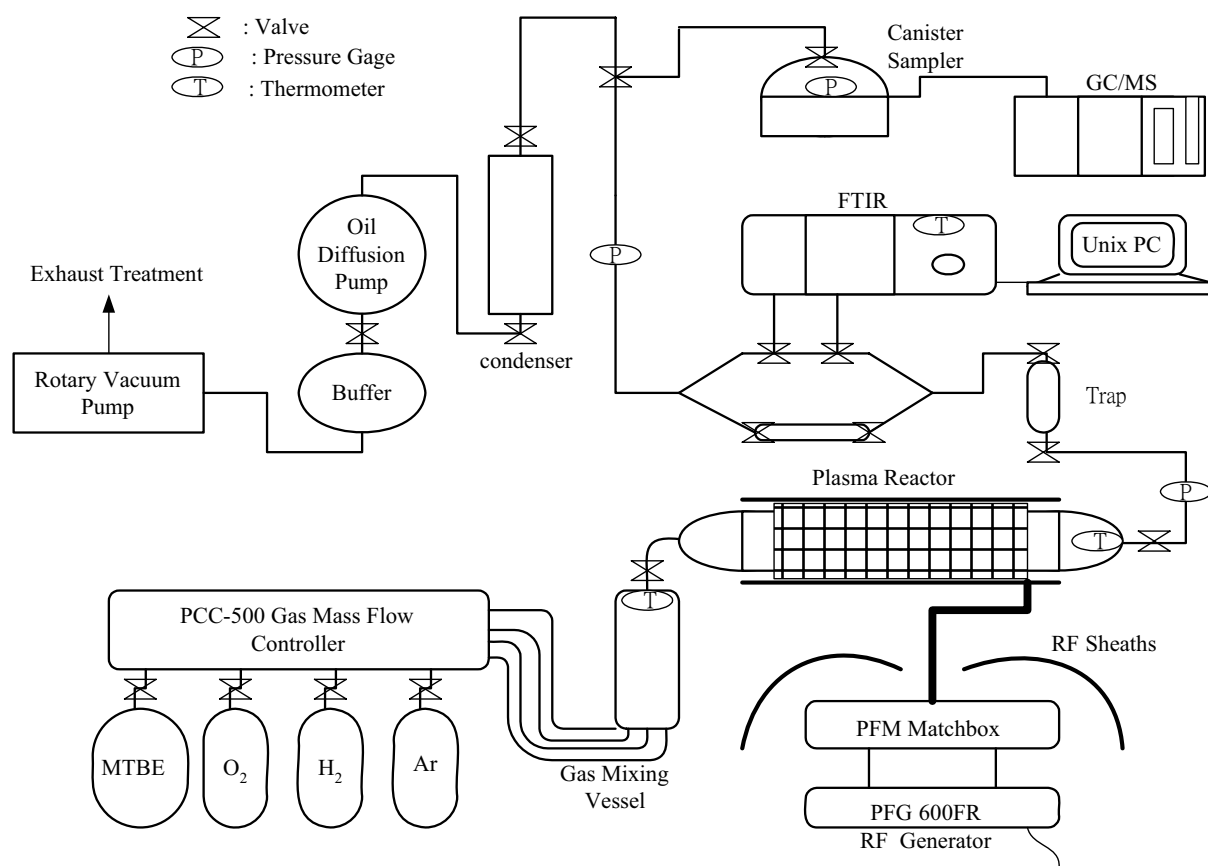


Fig. 1. Schematic of the Radio-frequency plasma system.

3304 1/cm), C₂H₄ (949, 987, 1444, 2987, 3124 1/cm), CH₃OH (1013, 1032, 1056, 1345, 1453, 2972, 3680 1/cm), *i*-C₄H₈ (889, 2944, 2979, 3088 1/cm), *i*-C₄H₁₀ (1478, 2967, 2952 1/cm), HCHO (1745, 2897 1/cm), CH₃CHO (1761, 1741, 1734, 2726 1/cm), and MTBE (855, 1097, 1209, 1368, 2835, 2917, 2989 1/cm).

Each run took at least 13 min and the results showed that steady-state conditions were obtained in the effluent after 9.8 min. The reported data are mean values measured under steady-state conditions. In this study, the MTBE decomposition efficiency (%), η_{MTBE} , is defined as follows.

$$\eta_{\text{MTBE}} = [(C_{\text{MTBE}} - C_{\text{exit}})/(C_{\text{MTBE}})] \times 100\% \quad (1)$$

where C_{MTBE} is the influent concentration of MTBE (%) and C_{exit} is the effluent concentration of MTBE (%). FT-IR quantification data were also checked using a carbon balance to evaluate the effects of both deposition and condensation in the sampling and analyzing apparatus. In the MTBE/H₂/Ar plasma system, the carbon balance (CB) is defined as follows.

$$CB = \frac{\sum_{i=1}^n [(C_{\text{out}})_i \times (N_i)]}{C_{\text{MTBE}}} \quad (2)$$

where $(C_{\text{out}})_i$ is the concentration of the *i*th species in the effluent (%); N_i is the number of carbon atoms in the chemical formula for the *i*th species in the effluent; n is the total number of species in the effluent, and C_{MTBE} is the MTBE influent concentration (%).

RESULTS AND DISCUSSION

Steady State in the RF Reactor

A steady-state was considered to have been entered when relatively constant decomposition fractions and absorbance-peaks of product species were obtained by FT-IR with particular operational parameters (including gas feeding concentration, operational pressure, total gas flow rate and input power). Each experimental run 13 min and the effluent concentrations of species were monitored by the FTIR throughout the reaction. The results of all experiments indicate that the steady-state conditions were reached in the effluent after 9.8 minutes. Additionally, all samples of the deposit in all systems were stored in the reactor at steady state. Notably, data reported herein are based on mean values measured after a steady-state had been reached.

In the steady state, the final products left the reactor and identified; they were CO, CO₂, CH₄, C₂H₂, C₂H₄, CH₃OH, *i*-C₄H₈, *i*-C₄H₁₀, HCHO, CH₃CHO, and MTBE.

Formation of Species

The species produced in the plasmachemical reactions are characterized by their simplicity and stability, because that both the short residence time and the short quenching time in a low-pressure environment limit the possibility of

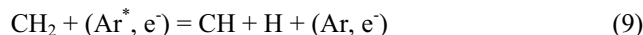
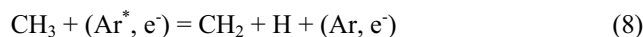
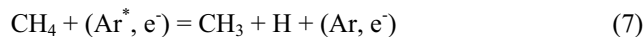
the operation of slow multistep mechanisms crucial to the formation of complex compounds. For example, in the authors' earlier radio-frequency plasma studies (Wang *et al.*, 1999b), the main final products in the C₂HCl₃/Ar RF plasma were CO, CO₂, HCl, and Cl₂, and the main products in the CCl₂F₂/H₂/Ar plasma were HF, HCl, CH₄ and C₂H₂ (Wang *et al.*, 1999b).

In this study, the detected species formed at the exit of the RF reactor were classified into four groups. The first group, C_xH_y, includes CH₄, C₂H₂, C₂H₄, *i*-C₄H₈, and *i*-C₄H₁₀. The second group, Coy, includes CO and CO₂. The third group, R-CHO, includes HCHO and CH₃CHO. The fourth group, R-OH, includes only CH₃OH.

In the plasma reactor, the initial reactions involved the excitation of Ar, as follows.



In the RF plasma zone, MTBE was immediately decomposed and CH₃ free radicals were produced directly by breaking the C-C bond. Then, in the plasma reactor, CH₄ is formed and decomposes as follows.

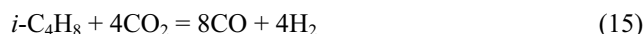
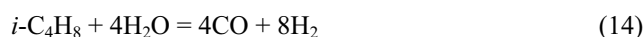


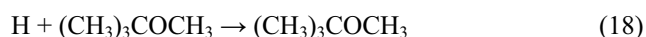
In Eq. (6), M refers to third-molecules in the RF plasma reactor during the reaction.

The production of C₂H₂ is associated with the depletion of both C₂H₄ and CH₄. In the plasma reactor, C₂H₂ can form and decompose, as follows (Wang *et al.*, 1999a).



Additionally, the important reforming reactions of *iso*-butene are as follows (Anderson, 2000).





Effect of Input Power on Decomposition of MTBE

Experiments were performed to examine the dependence of η_{MTBE} , CB and the fraction of total-input carbon converted on the input power from 20 to 70W; the H_2/MTBE ratio was 7.5; the operational pressure was 20 Torr, and the influent concentration of MTBE was 5.0%.

Fig. 2(A) indicated that η_{MTBE} increased with the input power. However, the experimental results showed that CB declined as the input power in the RF plasma reactor increased (Fig. 2(B)). This finding is associated with the formation of a deposit on the inner wall of the RF plasma reactor in contact with the flue gas in the MTBE/ H_2 /Ar plasma.

Fig. 2(C) indicates that the mole fractions of CH_4 , C_2H_2 and C_2H_4 increased with the input power. The results showed that more CH_4 was formed than C_2H_2 or C_2H_4 . The fraction of total input carbon converted into CH_4 , C_2H_2 or C_2H_4 ($F_{\text{CH}_4+\text{C}_2\text{H}_2+\text{C}_2\text{H}_4}$) increased with the input power (Fig.

2(D)). A high input power resulted in both the high collision frequency of reactants and the ease of formation of excited species, associated with the Maxwellian electron energy distribution function (EEDF) (Boenig, 1988); the increase in the mean electron energy increase η_{MTBE} and $F_{\text{CH}_4+\text{C}_2\text{H}_2+\text{C}_2\text{H}_4}$ in the reactor.

Both carbon monoxide (CO) and carbon dioxide (CO_2) were detected in the effluent of the plasma reactor. Fig. 3(A) indicates that less CO_2 and more CO were formed as the input power increased. The number of effective electrons increased with input power. The product CO_2 further reacted with electrons to generate CO as follows (Chang and Yu, 2001).



The fraction of total input carbon converted into CO + CO_2 ($F_{\text{CO}+\text{CO}_2}$) increased with the input power (Fig. 3(B)). The effective energy that enter in the reaction zone increased with the input power and promoted the reaction,

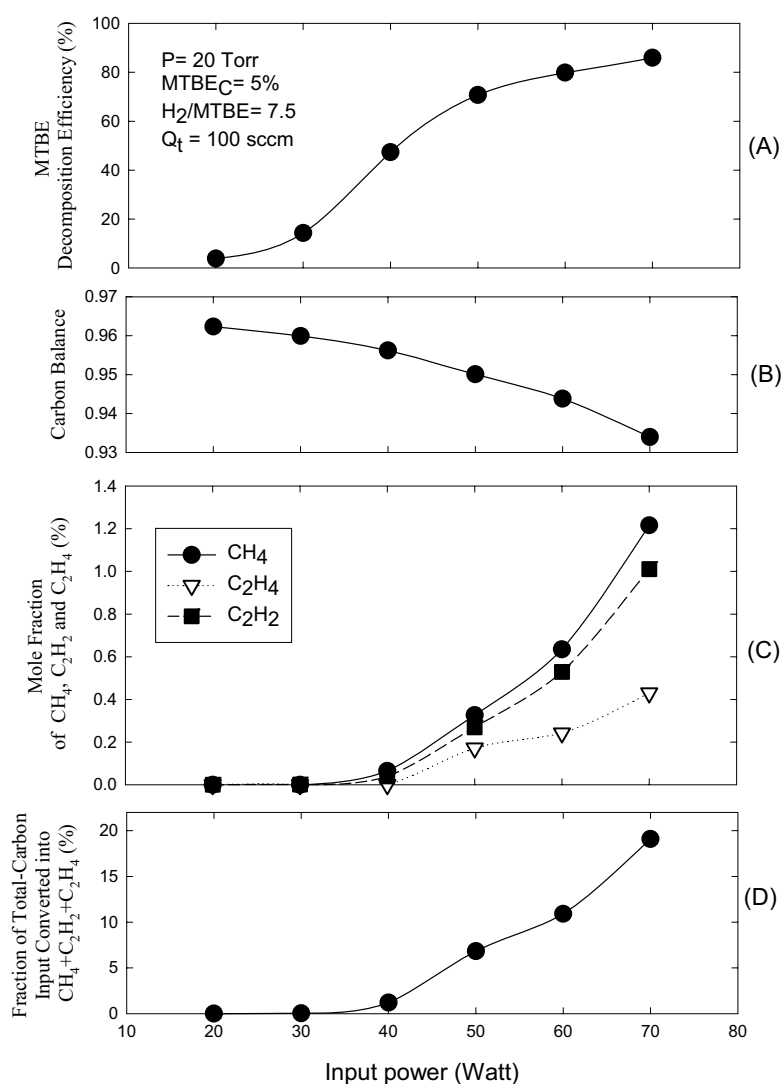


Fig. 2. (A) MTBE decomposition efficiency, η_{MTBE} (%). (B) Carbon balance. (C) Mole fractions of CH_4 , C_2H_2 , and C_2H_4 (%). (D) Fraction of total input carbon converted into $\text{CH}_4 + \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$ (%) at various input powers.

increasing $F_{\text{CO}+\text{CO}_2}$. MTBE is produced by the liquid-phase addition of methanol to form isobutene (Fite *et al.*, 1998). The MTBE synthesis reaction is exothermic ($\Delta H_r = -9.5$ Kcal/mol) and was performed over an acidic ion-exchange resin at operating temperatures between 40°C and 80°C (Girolamo and Tagliabue, 1999). Hence, that both *iso*-butane (*iso*-C₄H₁₀) and *iso*-butene (*iso*-C₄H₈) were detected in the effluent gas streams of the MTBE/H₂/Ar plasma system is not surprising. Fig. 3(C) plots that the trends in the formation of *iso*-butane (*iso*-C₄H₁₀) and *iso*-butene (*iso*-C₄H₈) are similar. The formation of *iso*-C₄H₁₀ and *iso*-C₄H₈ increased with the input power from 20 to 60W and then declined slightly as power increased beyond 60W. The fraction of total input carbon converted into *iso*-C₄H₁₀ + *iso*-C₄H₈, was maximum at an input power of 40W, and was then 64.3% (Fig. 3(D)).

Effect of H₂/MTBE Ratio on Decomposition of MTBE

Experiments were performed to determine the dependence

of η_{MTBE} , CB and the fraction of input carbon converted on the H₂/MTBE ratio from 1.0 to 10 at an input power of 50W, an operational pressure of 20 Torr, and an MTBE influent concentration of 5.0%. Fig. 4(A) indicated that η_{MTBE} decreased as the H₂/MTBE ratio increased. Argon promoted the dissociation of MTBE because it is easily excited and ionized. Hence, at a fixed total flow rate of 100 sccm, a higher H₂/MTBE ratio yielded a decreased η_{MTBE} . Fig. 4(B) indicated that CB increased with the H₂/MTBE ratio from 1.0 to 7.5 and was then remained at approximately 0.96 as the H₂/MTBE ratio increased from 8.5 to 10, due to a rapid fall in the decomposition of MTBE. In this work, a lower CB value at a lower H₂/MTBE ratio accompanied a larger η_{MTBE} . Fig. 4(C) plots the mole fractions of CH₄, C₂H₂ and C₂H₄ against H₂/MTBE ratio. The results show that the concentrations of CH₄, C₂H₂ and C₂H₄ all decreased as the H₂/MTBE ratio increased. More CH₄ than C₂H₂ or C₂H₄ was formed. A higher H₂/MTBE ratio or a lower Ar concentration reduced the probability of

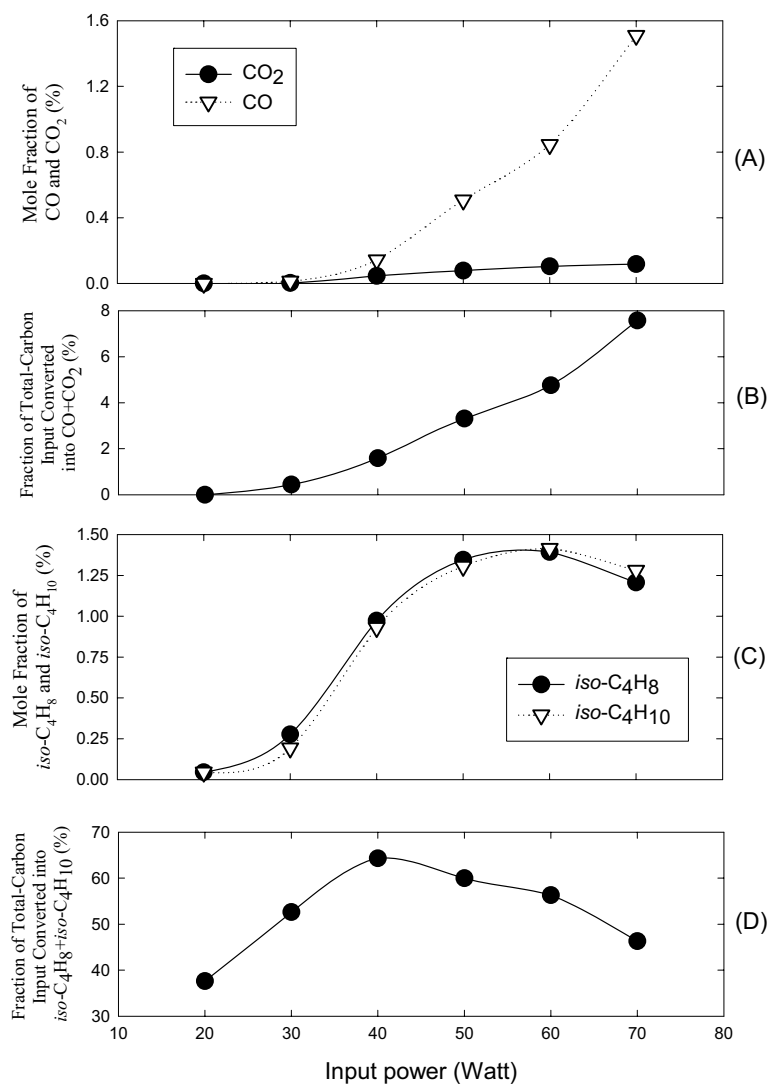


Fig. 3. (A) Mole fractions of CO and CO₂ (%). (B) Fraction of total input carbon converted into CO + CO₂ (%). (C) Mole fraction of *iso*-C₄H₈ and *iso*-C₄H₁₀ (%). (D) Fraction of total input carbon converted into *iso*-C₄H₈+*iso*-C₄H₁₀ (%) at various input powers.

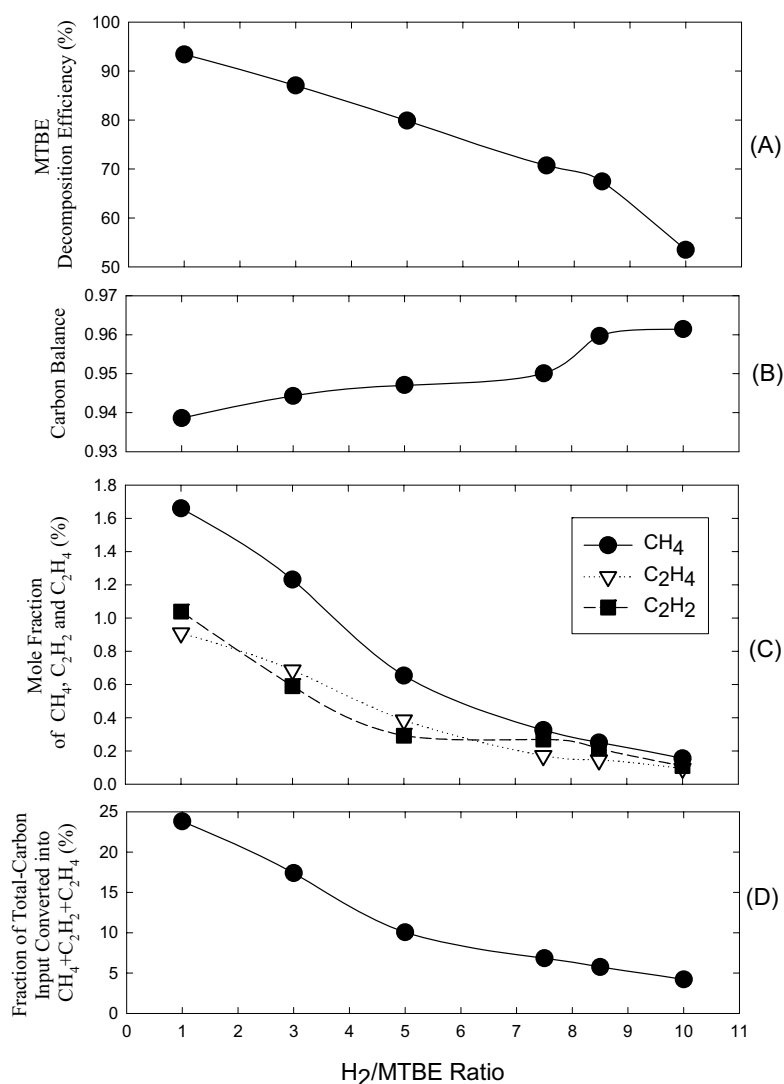


Fig. 4. (A) MTBE decomposition efficiency, η_{MTBE} (%). (B) Carbon balance. (C) Mole fractions of CH₄, C₂H₂, and C₂H₄ (%). (D) Fraction of total input carbon converted into CH₄+C₂H₂+C₂H₄ (%) at various H₂/MTBE ratios.

converting the formed CH₄ into more stable C₂H₄ and C₂H₂. For example, the mole fractions of CH₄, C₂H₂ and C₂H₄ were all below 0.2% when the H₂/MTBE ratio was ten. Fig. 5(A) indicates that the amount of CO formed fell sharply as the H₂/MTBE ratio increased but the amount of CO₂ formed was constant as the H₂/MTBE ratio increased. F_{CO+CO₂} fell as the H₂/MTBE ratio increased (Fig. 5(B)).

Fig. 5(C) shows that the mole fractions of both *iso*-C₄H₁₀ and *iso*-C₄H₈ were maximum at an H₂/MTBE ratio of 5.0, as the H₂/MTBE ratio was increased from 1.0 to 10, which finding is explained by two facts about the MTBE/H₂/Ar plasma reactor. First, the formations of *iso*-C₄H₁₀ and *iso*-C₄H₈ are exothermic. Second, the mean effective electron energy is reduced by both the increase in the H₂/MTBE ratio and the decrease in the amount of excited Ar in the plasma reactor. Adding a little hydrogen to vary the H₂/MTBE ratio from 1.0 to 5.0 causes the gas temperature in the reactor to fall from 524K to 486K, promoting the exothermic formation of *iso*-C₄H₁₀ and *iso*-C₄H₈. Hence, the mole fractions of *iso*-C₄H₁₀ and *iso*-C₄H₈ increased with the

H₂/MTBE ratio from 1.0 to 5.0. However, as the H₂/MTBE ratio increases from 5.0 to 10, the effect of the fall in mean effective electron energy on the formation of *iso*-C₄H₁₀ and *iso*-C₄H₈ exceeds that of a fall in the temperature of the gas in the reactor. Hence, the mole fractions of *iso*-C₄H₁₀ and *iso*-C₄H₈ declined as the H₂/MTBE ratio increased from 5.0 to 10. Fig. 5(D) reveals that the fraction of total input carbon converted into *iso*-C₄H₁₀ + *iso*-C₄H₈ increases with the H₂/MTBE ratio and exceeds 60% when the H₂/MTBE ratio exceeds 7.5. Moreover, the conversion rate is as high as 65.5% when the ratio is ten.

Effect of Influent Concentration MTBE on Decomposition of MTBE

Experiments were performed to elucidate the dependence of η_{MTBE} , CB and the fraction of input carbon converted on the influent concentration MTBE from 1 to 5% at an H₂/MTBE ratio of 7.5, an operational pressure of 20 Torr, and an input power of 50W. Fig. 6 indicates that η_{MTBE} , CB and F_{CH₄+C₂H₂+C₂H₄} all declined as the influent concentration

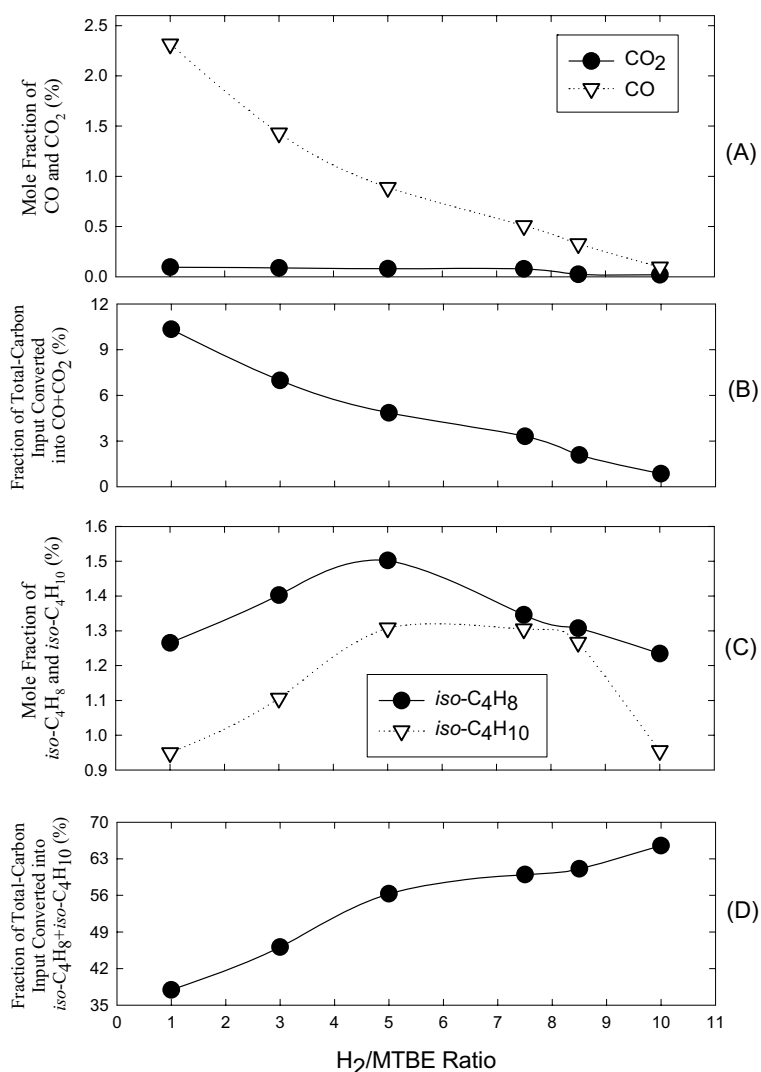


Fig. 5. (A) Mole fractions of CO and CO₂ (%). (B) Fraction of total input carbon converted into CO + CO₂ (%). (C) Mole fractions of *iso*-C₄H₈ and *iso*-C₄H₁₀ (%). (D) Fraction of total input carbon converted into *iso*-C₄H₈+*iso*-C₄H₁₀ (%) at various H₂/MTBE ratios.

of MTBE increased (Figs. 6(A), 6(B) and 6(D)). Increasing the MTBE influent concentration increases the molecular density; reduces the concentration of excited argon molecules, and reduces the frequency of collision of effective reactants. These changes together reduce η_{MTBE} and $F_{\text{CH}_4+\text{C}_2\text{H}_2+\text{C}_2\text{H}_4}$. Additionally, Fig. 6(C) shows that the mole fractions of CH₄ and C₂H₄ increased slowly with MTBE influent concentration. However, the mole fraction of C₂H₂ initially increased and then decreased as the MTBE concentration was increased from 2 to 5%. Fig. 7(A) indicates that the amount of CO formed increased slightly with MTBE concentration, when the CO₂ concentration was maintained at 0.1%. More CO than CO₂ was formed. Fig. 7(B) indicated that $F_{\text{CO}+\text{CO}_2}$ fell as the MTBE concentration increased. Figs. 7(C) and 7(D) indicated that the mole fractions of both *iso*-C₄H₁₀ and *iso*-C₄H₈ and the fraction of total input carbon converted into *iso*-C₄H₁₀ + *iso*-C₄H₈ increased with influent concentration of MTBE. More reactants and a higher MTBE concentration promoted the production of *iso*-C₄H₁₀ and *iso*-C₄H₈. Additionally, the

experimental results reveal that the fraction of total input carbon converted into *iso*-C₄H₁₀ + *iso*-C₄H₈ exceeded 55% when the influent concentration of MTBE exceeded 4%.

Soot Formation in the RF Plasma Reactor

Soot formation was also found in several case studies associated with plasma decomposing reaction. Lee *et al.* (1996) indicated more soot was found in the plasma reactor when the input power wattage was higher than 60 W. Because high concentrations of C₂Cl₄, CHCl₃ and CCl₄ were detected and because copper inner-electrode might act as catalyst, the most possible pathways for the COCl₂ formation were C₂Cl₄ + OH, C₂Cl₃ + O₂, CHCl₃ + O, CHCl₂ + O, CCl₃ + O and CO + Cl₂. In the BF₃/O₂/Ar RF plasma reactor, Wang *et al.* (2003) also reported the competitive reaction between O₂ and BF₃ and O₂ and H₂ made the deposition thinner than in the BF₃/O₂/Ar RF plasma system, in which fewer B₂O₃ particles were formed. Wang *et al.* (2003) also reported the deposition in the BF₃/H₂/Ar system, with tungsten as a catalyst in the reactor.

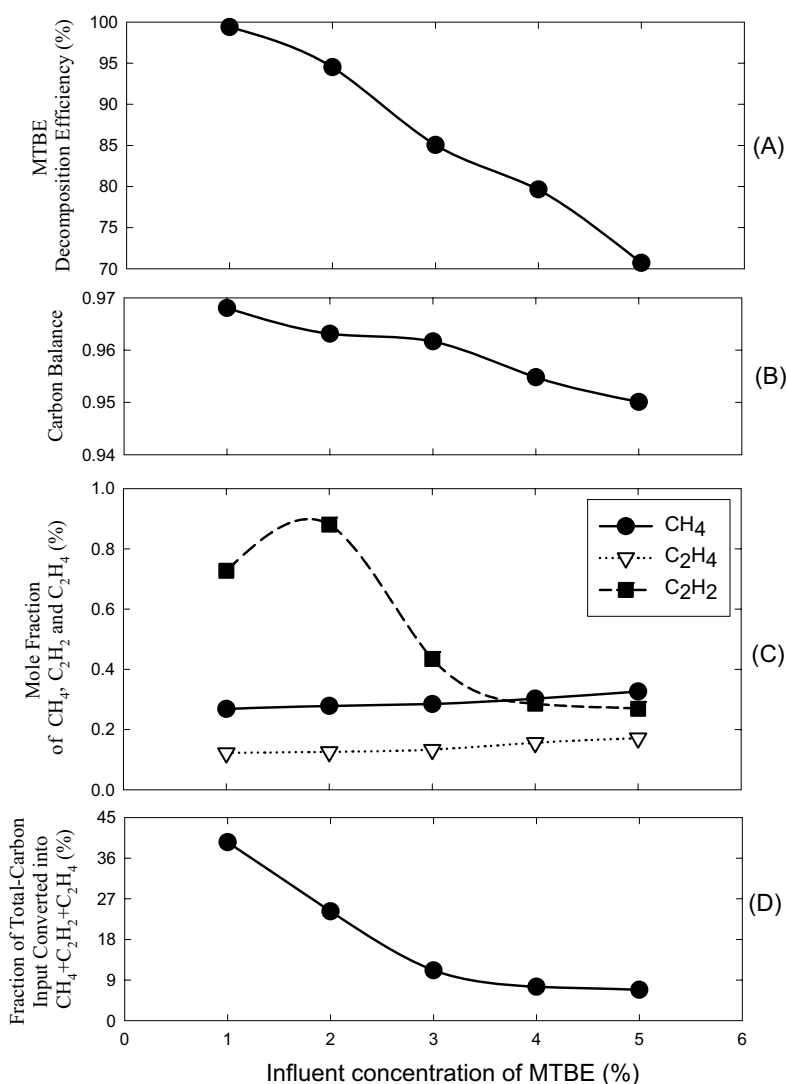


Fig. 6. (A) MTBE decomposition efficiency, η_{MTBE} (%). (B) Carbon balance. (C) Mole fractions of CH_4 , C_2H_2 , and C_2H_4 (%). (D) Fraction of total input carbon converted into $\text{CH}_4 + \text{C}_2\text{H}_2 + \text{C}_2\text{H}_4$ (%) at various influent concentrations of MTBE.

Interestingly, cobweb deposition formed on the surface of the reactor. Although the η_{BF_3} was not favorable, many fine particles were still generated in the system, resulting in the formation of deposition on the surface of the reactor. Accordingly, much more attention should be paid to the generation of fine particles in such systems in the ion implantation industry (Wang *et al.*, 2003). Similarly, 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 (Liao *et al.*, 2003).

In this work, increasing the input power or the MTBE influent concentration reduced the carbon balance in the MTBE/ H_2 /Ar radio frequency plasma environment, because deposits formed on the inside wall of the reactor. When the input power exceeded 50 W, a light brown film was deposited on the inside and downstream of the plasma reactor. Under these deposition conditions, the input power density was calculated usually to exceed $0.55\text{W}/\text{cm}^3$. The chemical analysis (ESCA, ESCA-210) by electron

spectroscopy of the elemental content of this dark brown film deposition revealed the presence of carbon and oxygen. The photograph of the deposit peeled from downstream of the plasma reactor, obtained by scanning electron microscopy (SEM, JXA840A) with and without H_2 added revealed that larger and looser crystals were formed when H_2 was added (Fig. 8). The difference between the configuration of the aggregates may follow from the difference between the mechanisms associated with a hydrogenated and a non-hydrogenated RF plasma environment. In the MTBE/Ar plasma reaction, polymerization proceeded mainly by an ion-molecule mechanism, while a radical mechanism dominated the MTBE/ H_2 /Ar plasma reaction, because of the addition of hydrogen pool. Moreover, analysis of the deposit in the reactor revealed that the total concentration of the 21 polycyclic aromatic hydrocarbons (PAHs) (Sheu *et al.*, 1996) was around $82.8\ \mu\text{g}/\text{g}$. PAHs were formed possibly via the consecutive addition and cyclization of hydrocarbon free radicals (Wang *et al.*, 1999a). Moreover, such soot

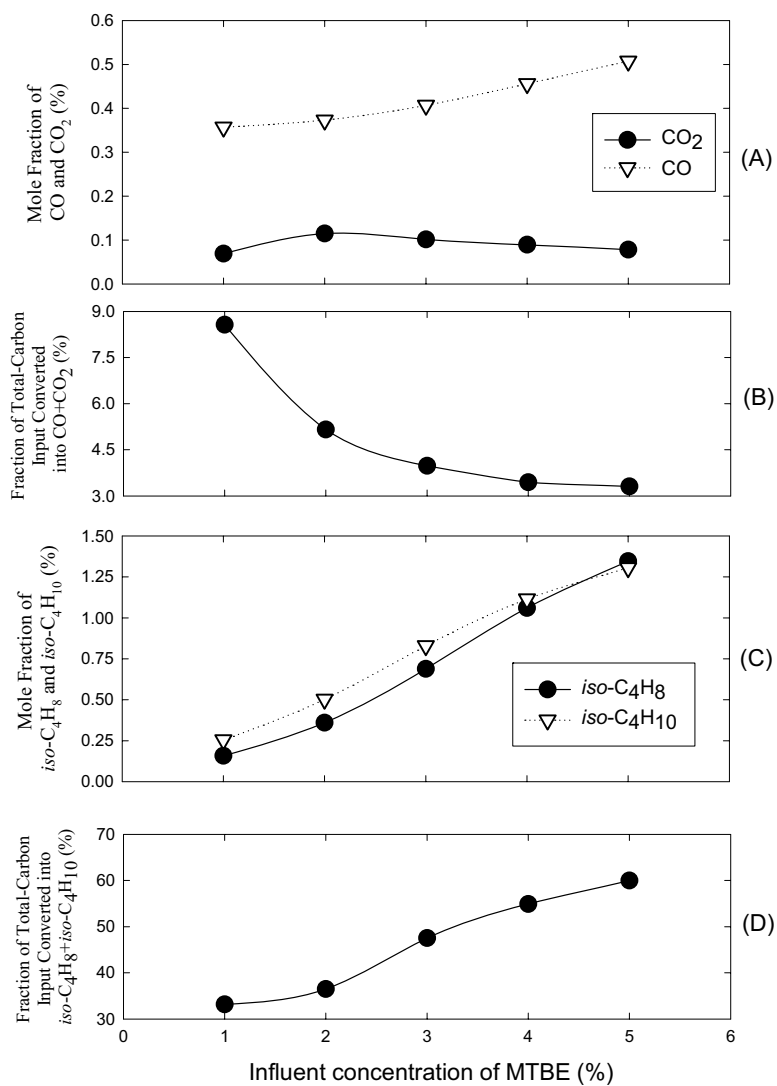
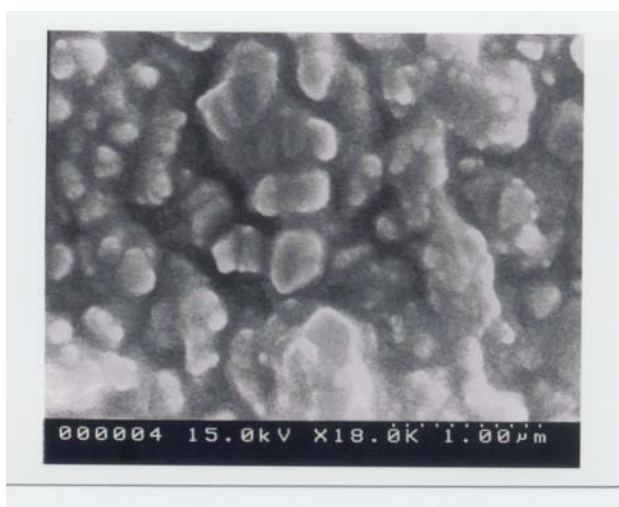
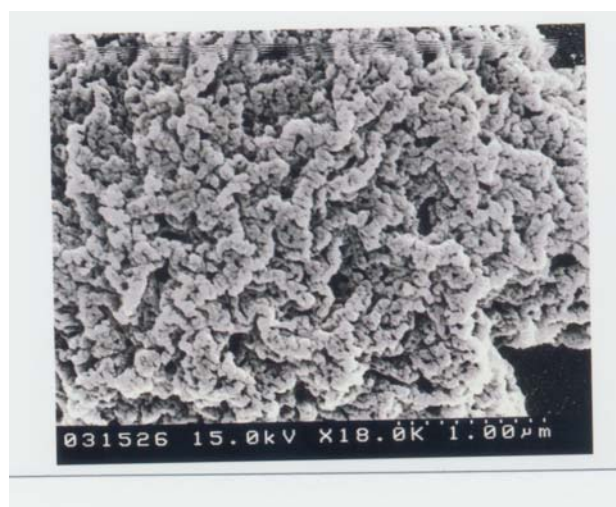


Fig. 7. (A) Mole fractions of CO and CO₂ (%). (B) Fraction of total input carbon converted into CO + CO₂ (%). (C) Mole fractions of *iso*-C₄H₈ and *iso*-C₄H₁₀ (%). (D) Fraction of total input carbon converted into *iso*-C₄H₈+*iso*-C₄H₁₀ (%) at various influent concentrations of MTBE.



(A)



(B)

Fig. 8. (A) Deposition without H₂. (B) Deposition with H₂

formation in the RF plasma reactor is different from the particle depositions from others combustion process in atmospheric environment (Chiu *et al.*, 2011; Kim *et al.*, 2011; Ruttanachot *et al.*, 2011)

In the 1970s, MTBE represented the great hope for replacing tetraethyllead as the main antiknock additive in gasoline. However, people are now trying to work MTBE out of the motor fuel systems. Applying RF plasma and adding hydrogen can convert MTBE into CH₄, C₂H₄, C₂H₂, *iso*-C₄H₈ and *iso*-C₄H₁₀.

CONCLUSIONS

From many previously research studies, we understand that there are four types of the application in the RF plasma reactors can be discussed, including: (i) **Application I.**: Converting methane, decomposing carbon dioxide, ethoxyethane, and ethylene oxide; (ii) **Application II.**: Decomposing methyl chloride, 1,1-C₂H₂Cl₂, and CH₂Cl₂; (iii) **Application III.**: Decomposing dichlorodifluoromethane, CHF₃, CH₂F₂, CCl₂F₂, and BF₃; (iv) **Application IV.**: Decomposing dichlorodifluoromethane, CH₃SH, CS₂, SF₆, and SF₆ + H₂S mixture. Up to now, the RF plasma reactor is a potentially important technology for decomposition and gas treatment in many laboratories. In this study, the radio-frequency plasma reactor provides enough energy to break down MTBE and allows the plasma parameters to be controlled at an MTBE feeding concentration of up to 5%. In this study, the fraction of total input carbon converted into *iso*-butane and *iso*-butene (F_{*i*-C₄H₁₀+*i*-C₄H₈}) increases with the H₂/MTBE ratio and the influent concentration of MTBE in the MTBE/H₂/Ar plasma environment. Experimental results indicated that η_{MTBE} exceeds 99.4% and F_{CH₄+C₂H₂+C₂H₄} exceeds 39.5% at an input power of 50 W, H₂/MTBE ratio of 7.5, an operational pressure of 20 Torr, and influent concentration of MTBE of 1%. Additionally, F_{*i*-C₄H₁₀+*i*-C₄H₈} can reach 65.5% at an input power of 50 W, an H₂/MTBE ratio of 10, an operational pressure of 20 Torr, and an influent concentration of MTBE of 5%. The results obtained herein show that MTBE can be significantly decomposed and converted into CH₄, C₂H₂, and C₂H₄ in an MTBE/Ar/H₂ mixture. Moreover, in this study, the detected species formed at the exit of the RF reactor were classified into four groups. The first group, C_xH_y, includes CH₄, C₂H₂, C₂H₄, *i*-C₄H₈, and *i*-C₄H₁₀. The second group, C_oy, includes CO and CO₂. The third group, R-CHO, includes HCHO and CH₃CHO. The fourth group, R-OH, includes only CH₃OH. As far as the mechanism of decomposition for MTBE, MTBE was immediately decomposed in the plasma reactor, and then CH₃ free radicals were produced directly by breaking the C-C bond. Then, in the plasma reactor, CH₄ is formed and decomposes. Besides, the production of C₂H₂ is associated with the depletion of both C₂H₄ and CH₄. In the reactor, the important production of *iso*-butene may through several pathways, including: *i*-C₄H₈ + 4H₂O = 4CO + 8H₂; *i*-C₄H₈ + 4CO₂ = 8CO + 4H₂; CH₃OH + *i*-C₄H₈ = (CH₃)₃COCH₃ (MTBE); (CH₃)₃COCH₃ + *hν* → CH₃OH + *i*-C₄H₈; and H + (CH₃)₃COCH₃ → (CH₃)₃COCH₃.

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NOTATION

η _{MTBE}	MTBE decomposition efficiency (%);
W _D	Power density in the plasma (W/cm ³);
C _{MTBE}	MTBE feeding concentration (%);
M _{CH₄}	Mole fraction of CH ₄ (%);
M _{C₂H₄}	Mole fraction of C ₂ H ₄ (%);
M _{C₂H₂}	Mole fraction of C ₂ H ₂ (%);
M _{CO}	Mole fraction of CO (%);
M _{CO₂}	Mole fraction of CO ₂ (%);
M _{CH₃OH}	Mole fraction of CH ₃ OH (%);
M _{HCHO}	Mole fraction of HCHO (%);
M _{CH₃CHO}	Mole fraction of CH ₃ CHO (%);
M _{<i>i</i>-C₄H₈}	Mole fraction of <i>iso</i> -butene (%);
M _{<i>i</i>-C₄H₁₀}	Mole fraction of <i>iso</i> -butane (%);
F _{CH₄}	Fraction of total input carbon converted into CH ₄ (%);
F _{C₂H₄}	Fraction of total input carbon converted into C ₂ H ₄ (%);
F _{C₂H₂}	Fraction of total input carbon converted into C ₂ H ₂ (%);
F _{CO}	Fraction of total input carbon converted into CO (%);
F _{CO₂}	Fraction of total input carbon converted into CO ₂ (%);
F _{CH₃OH}	Fraction of total input carbon converted into CH ₃ OH (%);
F _{HCHO}	Fraction of total input carbon converted into HCHO (%);
F _{CH₃CHO}	Fraction of total input carbon converted into CH ₃ CHO (%);
F _{<i>i</i>-C₄H₈}	Fraction of total input carbon converted into <i>iso</i> -butene (%);
F _{<i>i</i>-C₄H₁₀}	Fraction of total input carbon converted into <i>iso</i> -butane (%).

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