Conversion of SO_2 into Elemental Sulfur by Using the RF Plasma Technique

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*This study demonstrates a new approach for converting SO_2 into elemental sulfur by adding CH_4 in a radio-frequency (RF) plasma reactor. With the applied power (*P*) of the RF reactor specified at 90 W and operating pressure set at 4000 N/m^2, it was found that as the CH_4/SO_2 ratio (*R*) was increased from 0.3 to 1.0, most sulfur-containing products were in the form of elemental sulfur. While* R *was increased from 1 to 2, the content of elemental sulfur was decreased significantly, but CS_2 was increased dramatically. While* R *was increased from 2 to 3, both elemental sulfur and CS_2 contents became quite comparable. Nevertheless, it was found that both H_2 and CO (that is, syngas) were the main nonsulfur-containing products under all testing conditions. These results indicate that the use of the RF plasma technique was not only beneficial to convert SO_2, but also was able to convert CH_4 into useful materials. For* $R = 0$ *(that is, no CH_4 was introduced), it was found that the SO_2 conversion (i.e., η_{SO_2}) = 0.084, indicating that the RF plasma process was inadequate to convert pure SO_2 without adding CH_4 as a reducing agent. While* R *was increased to 2, it was found that η_{SO_2} was improved significantly to 0.968 accompanied with $\eta_{CH_4} = 0.999$. 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. Based on these, this study suggests that the operating condition of* $R = 2$ *and* $P = 90$ *W would be the most appropriate combination for SO_2 conversion.* © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 524–529, 2004

Keywords: sulfur dioxide, methane, radio-frequency plasma, elemental sulfur, enviromental engineering, energy, plasma

Introduction

For many industrial processes, such as petrochemical and nonferrous metal smelting processes, a number of regenerable flue-gas desulfurization (FGD) processes have been developed for the recovery of sulfur content from the high concentrations of SO_2 (Ratcliffe and Pap, 1980). Theoretically, SO_2 can be converted into several recovery forms, including sulfuric acid, elemental sulfur, liquid sulfur dioxide, and carbon disulfide, which are strongly dependent on the selected approaches (Murthy et al., 1976; Bejarano et al., 2001). Among various FGD processes, the approach associated with the reduction of SO_2 to

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elemental sulfur has been widely used and requires the use of some effective reducing agents, such as CO and H_2, and CH_4, to react with SO_2 (Ratcliffe and Pap, 1980; Murthy et al., 1976). The reaction associated with the use of CO and H_2 for reducing SO_2 to elemental sulfur is

$$1.5\ SO_2 + CO + 2H_2 = 0.75\ S_{2(g)} + CO_2 + 2\ H_2O \quad (1a)$$

However, it should be noted that this process usually requires the use of CH_4 for the generation of CO and H_2 based on the following reaction:

$$CH_4 + 0.5\ O_2 = CO + 2H_2 \quad (1b)$$

On the other hand, the conversion of SO_2 can also be carried out by directly using CH_4 according to the following reaction:

$$2\ SO_2 + CH_4 = CO_2 + H_2O + 2\,[S] \quad (2a)$$

where [S] represents the various resulting elemental forms of sulfur species including S_2, S_6, and S_8. However, it should be noted that it is not possible to achieve the preceding reaction at a low temperature. Even at a high temperature of 750°C, a study conducted by Sarlis and Berk have clearly indicated that no reaction could be obtained (Sarlis and Berk, 1988). However, the reducing process just cited can be improved by adding appropriate catalysts such as Al_2O_3, Mo/γ-Al_2O_3, Co_3O_4/γ-Al_2O_3, and CeO_2-based catalysts (Sarlis and Berk, 1988, 1996; Yu et al., 1997; Zhu et al., 1999). But there are several problems that still need to be solved in this approach. These include: (1) the sulfur-poisoning effect might eliminate the availability of catalyst, (2) catalysts need to be regenerated, and (3) waste catalysts need to be treated. In addition, it should be noted that this approach is also accompanied by the following parallel reaction

$$SO_2 + CH_4 = H_2S + CO + H_2O \quad (2b)$$

Obviously, the generation of H_2S has not only needed the use of additional reactors for treatment, but also limited the use of the approach (Yu et al., 1997; Zhu et al., 1999; Nekrich et al., 1978).

Besides the reducing approach just discussed, plasmalysis technology has also become available for the conversion of a low concentration of SO_2 into sulfuric acid (Frank, 1992; Van Veldhuizen et al., 1998; Chang et al., 1992). In order to enhance the SO_2 conversion and to reduce the corrosion caused by sulfuric acid, ammonia is usually used to neutralize the generated sulfur acid to form ammonium sulfate ($(NH_4)_2SO_4$). Indeed, ammonium sulfate does cause fewer transportation problems than sulfuric acid, but the coeffluent of unreated NH_3 from the preceding process might cause another serious odor problem.

In our previous studies, we have successfully used a 13.56-MHz radio-frequency (RF) plasma to convert both CH_3SH and CS_2 at room temperature (Tsai et al., 2001, 2002). Results showed that CH_3SH could be converted primarily into SO_2 and CS_2 at oxygen-rich and nonoxygen conditions, respectively. The conversion reached 0.981 when the O_2/CH_3SH ratio equaled 3 and the applied power was 90 W (Tsai et al., 2001). As for the CS_2 conversion, the high purity of elemental sulfur could be recovered under the conditions where the O_2/CS_2 ratio = 0.6 (Tsai et al., 2002). Based on these findings, it is expected that the technology just discussed also might be applicable for converting SO_2 into elemental sulfur by reacting with an appropriate reducing agent (such as CH_4). Assuming that this technology could be developed, it will not only be beneficial to industries for recovering sulfur contents from percentage-grade SO_2 at room temperature, but also will provide a new approach without causing further H_2S processing steps, catalyst regeneration, catalyst disposal, and NH_3 odor problems.

Proposed reaction pathways

It is known that the RF plasma processes are associated with (1) the generation of energetic species to impact with SO_2 and CH_4, (2) the generation of O, SO, S, CH_3, CH_2, CH, and H free radicals as well as ions through the plasmalysis process (Fan et al., 1999; Reese et al., 1958), and (3) the reformation of elemental sulfur, CS_2, H_2, CO, CO_2, and OCS. In principle, the positive ions SO_2^+, SO^+, S^+, O_2^+, and O^+ could be produced during the electron ionization–dissociation processes (Reese et al., 1958). But it should be noted that these ionization–dissociation processes usually require a high appearance potential (>10 eV) (Cadez et al., 1983). Considering that the electron temperature for RF plasma is usually <10 eV, which leads to the degree of ionization becoming less significant (typical $<10^{-6}$) (Eliasson and Kogelschatz, 1991). Therefore, it can be expected that the contributions of positive ions to the reaction processes could be negligible. On the other hand, it also should be noted that the negative ions SO^-, O^-, and S^- were relatively less abundant than the positive ions due to the low electron attachment rates (Reese et al., 1958; Wang and Lee, 1986). Based on these findings, we proposed that the complex nature of the product compositions in the RF plasma process could be mainly contributed by the free-radical chain reactions.

In this study, the elemental sulfur first generated from the plasma process was in a gaseous form, then it diffused to and became attached on the wall to form polysulfur via the heterogeneous wall reactions. In addition, the formation of CS_2 could be mainly due to the produced CS reacted with S or S_2 (Bobrin et al., 1989). H_2 is formed primarily via the reformation of H with H or CH_2 or direct CH_4 dissociation. As for CH_x decomposed from CH_4, it is consumed mainly by O atoms to form major CO, which can further react with S to form OCS. The reactions associated with the formation of major products, along with their relevant rate constants at 298 K [$cm^3\ mole^{-1}\ s^{-1}$ or † (see Eqs. 3, 4a, and 5a) for $cm^6\ mole^{-2}\ s^{-1}$] have been known, including the following (Baulch et al., 1992; Devriendt et al., 1995; Saito et al., 1986; Howgate and Barr, 1973; Woiki and Roth, 1995; Karra and Senkan, 1988)

$$S + S + M = S_2 + M \qquad {}^\dagger k_3 = 8.68 \times 10^{14} \quad (3)$$

$$S + CS + M = CS_2 + M \qquad {}^\dagger k_{4a} = 9.57 \times 10^{14} \quad (4a)$$

$$S_2 + CS = CS_2 + S \qquad k_{4b} = 9.63 \times 10^{11} \quad (4b)$$

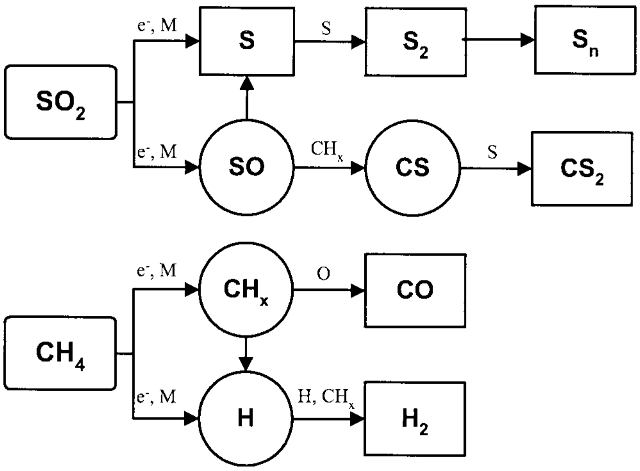

Figure 1. Proposed reaction pathways and major product for SO_2 conversion in RF plasma by CH_4 as a reducing agent.

$$H + H + M = H_2 + M \qquad {}^{\dagger}k_{5a} = 3.20 \times 10^{15} \qquad (5a)$$

$$H + CH_2 = H_2 + CH \qquad k_{5b} = 4.07 \times 10^{17} \qquad (5b)$$

$$CH + O = CO + H \qquad k_{6a} = 3.97 \times 10^{13} \qquad (6a)$$

$$CH_2 + O = CO + 2H \qquad k_{6b} = 8.00 \times 10^{13} \qquad (6b)$$

$$CO + S + Ar = OCS + Ar \qquad k_7 = 9.10 \times 10^{12}. \qquad (7)$$

Based on these equations, the major reaction pathways associated with the conversions of SO_2 and CH_4 in the $SO_2/CH_4/Ar$ RF plasma are proposed in this work and are shown in Figure 1. As shown in Figure 1, the plasma–chemical reactions involved could be classified into two major steps. The first step is associated with the generation of energetic species to impact with SO_2 and CH_4. The reaction rate constants in step 1 are strongly affected by the reduced field (electric field/gas density). The RF discharge is known with enough reduced field, and hence can be regarded as an efficient approach for the production of free radicals. Therefore, it is expected that the free-radical reactions dominated in the second step, thus yielding stable products. Based on these findings, we proposed that the total reaction rates for SO_2 conversion are mainly decided by T_e (electron temperature), $[e]$, and $[CH_4]$. However, it should be noted that the measurement of intermediates occurring in the plasma–chemical reaction process was difficult at this stage, which warrants the need for further confirmation in the future.

Experimental Section

In this study, CH_4 was selected as a reducing agent for converting percentage-grade SO_2 into elemental sulfur. The whole study was conducted on a laboratory-scale RF plasma reactor. The reactor was a vertical cylindrical glass tube with an inner diameter and length of 4.14 cm and 15 cm, respectively. This reactor was wrapped with two outer symmetrical copper electrodes (height = 5.4 cm), which were coupled to a 13.56-MHz RF generator (Fritz Huttinger Elektronik Gmbh, PFG 600, Germany) with a matching network (Matchbox PFM, Germany). A detailed description of this experimental apparatus appeared in our previous studies, and thus is not repeated here (Tsai et al., 2001, 2002). Three high-purity gases—CH_4, SO_2, and Ar—each provided by a gas cylinder with its gas flow rates regulated by a mass flow controller (Brooks, 5850 E, Japan), were first introduced into a gas mixer for mixing, then introduced into the RF plasma reactor to conduct the experiments. All experiments were done at room temperature (25°C). SO_2 was fed at concentration ($[SO_2]_{in}$), and was specified at 2% with inlet CH_4/SO_2 ratios (R) specified at 0–3.0, applied powers (P) specified at 15–120 W, and a total flow rate specified at 100 mL/min (at STP). The operating pressure of 4000 N/m^2 was used for generating discharge. A thermocouple was placed at the center of the rear part of the discharge zone in the reactor in order to measure the temperatures of effluent gases. Before each experiment was performed, the pressure of the reactor was evacuated to <0.1 N/m^2 by using a mechanical vacuum pump and a diffusion oil pump in order to ensure that the apparatus was free of contamination and that there was no leakage in the testing system.

After an experiment was conducted, the elemental sulfur, which was deposited on both the inner wall of the reactor and the glass wool sulfur trap, was quantified gravimetrically by using an electronic balance. The purity of the sulfur was determined by using an elemental analyzer (Elementar/vario EL). Sulfur structure was analyzed by X-ray diffraction (XRD) spectroscopy (Rigaku, D/Max III.V) with a CuK_α radiation ($2\theta = 5$–$80°$), and the appearance was observed by a scanning electron microscopy (SEM) (Hitachi, HF-2000, Japan). An on-line Fourier transform infrared spectrometer (Bio-Rad, FTS-7, USA) was connected for quantifying CH_4, SO_2, and end-products including CS_2, OCS, C_2H_2, C_2H_4, CO, and CO_2. In addition, the gaseous products were also injected into a gas chromatograph (HP, 5890, USA) equipped with a pulsed flame photometric detector to identify sulfur-containing compounds, and a thermal conductivity detector for identifying CO, CO_2, and H_2 in order to check the accuracy of the results. In this study, mass balances of sulfur and carbon species showed errors $<10\%$ both before and after the reactions.

The product compositions are based on molar concentrations of the effluent. The conversion of reactants (η) and a product's sulfur selectivity (SS) in this study are defined as follows

$$\eta_{SO_2} = ([SO_2]_{in} - [SO_2]_{out})/[SO_2]_{in}$$

$$\eta_{CH_4} = ([CH_4]_{in} - [CH_4]_{out})/[CH_4]_{in}$$

$$SS_S = [S_1]/([S_1] + [CS_2] + [OCS])$$

$$SS_{CS_2} = [CS_2]/([S_1] + [CS_2] + [OCS])$$

$$SS_{OCS} = [OCS]/([S_1] + [CS_2] + [OCS]).$$

Results and Discussion

Product compositions

Figure 2 shows the relationship between CH_4/SO_2 ratios (R; range = 0.3–3) and the product compositions for experiments conducted on $[SO_2]_{in} = 2\%$, $P = 90$ W, operating pressure =

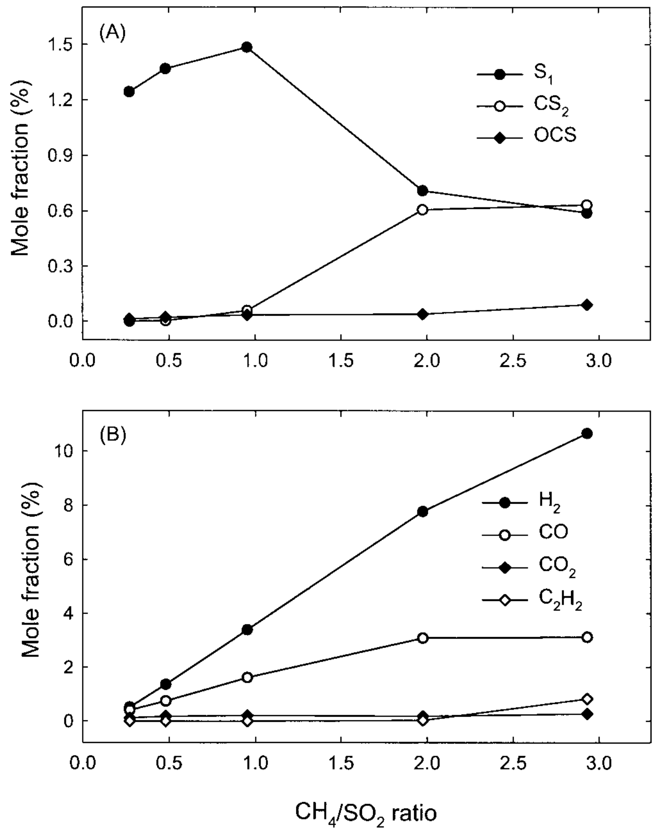

Figure 2. (A) Sulfur-containing, and (B) nonsulfur-containing product compositions for experiments conducted on various CH_4/SO_2 ratios with applied power at 90 W.

4000 N/m^2, and inlet temperature = 25°C. Results show that as R increased from 0.3 to 1.0, the sulfur products were presented mainly in the form of elemental sulfur, and its molar fractions $[S_1]$ were consistently increased from 1.240% to 1.485%, with the sulfur products of both $[CS_2]$ and [OCS] being less than 0.06% (Figure 2a). The low molar concentrations on both $[CS_2]$ and [OCS] might occur because almost all C atoms consumed by O atoms mainly formed CO, and hence resulted in the inhibition of their formations. The preceding inference can be confirmed by the results presented in Figure 2b. As shown in Figure 2b, we found that [CO] was increased significantly from 0.395% to 1.620%. Figure 2a also shows that the maximum yield of elemental sulfur was attained at $R = 1$. While R was increased from 1 to 2, we found that $[S_1]$ decreased from 1.485% to 0.711%, but $[CS_2]$ increased from 0.060% to 0.607%. These results might occur because C (provided by CH_4), which initially reacted primarily with O, was more apt to react with S to form CS_2 as R increased. Hence, as R was increased to 3, we found that $[S_1]$ decreased and $[CS_2]$ increased, and that both had quite comparable molar concentrations (~0.62%).

According to the studies, by using the catalytic process for the SO_2 reduction, it was found that the major products included not only CO_2, H_2O, and elemental sulfur (Eq. 2a), but also a toxic byproduct, H_2S, which was generated by the parallel reaction (Eq. 2b). In this study, we found that under no circumstance was H_2S detected. By taking both conditions of $R = 1$ and $R = 2$ as examples, this study yielded the following product compositions

$$SO_2 + CH_4 \rightarrow 0.74\, S_{1(s)} + 1.70\, H_2 + 0.81\, CO + 0.03\, CS_2 + 0.017\, OCS + 0.106\, CO_2 + 0.242\, H_2O \qquad (R = 1)$$

$$SO_2 + 2CH_4 \rightarrow 0.303\, CS_2 + 0.356\, S_{1(s)} + 3.88\, H_2 + 1.54\, CO + 0.020\, OCS + 0.091\, CO_2 + 0.156\, H_2O \qquad (R = 2)$$

Obviously, the product compositions obtained from this study were significantly different than those obtained from the catalytic process. No H_2S was found in this study, because the bonding in H_2S was too weak to remain stable in the RF plasma process. To date, it is known that many plasma technologies are available for the conversion of SO_2. However, it should be noted that the technologies just discussed are known to be associated with the conversion of low concentrations of SO_2 into sulfuric acid (Frank, 1992; Van Veldhuizen et al., 1998; Chang et al., 1992). But in this study we did not observe the long-chained H_2SO_4. This might be because the formation of the complex compound of H_2SO_4 was associated with slow multistep mechanisms that occurred with difficulty in the RF plasma process (Arno and Bevan, 1996).

In this study, we found that the other major products included H_2 and CO (i.e., syngas, the main reagents for the production of CH_3OH) (Figure 2b). A trace of light hydrocarbons was also detected only under the conditions at $R \geq 2$ (such as C_2H_2 was ~0%, 0.028%, and 0.735% at $R < 1$, $R = 2$, and $R = 3$, respectively). These results suggest that the use of the RF plasma technique was not only beneficial in converting SO_2 into elemental sulfur for recovery, but also was able to simultaneously convert CH_4 into useful materials (that is, the syngas).

Depositions analysis

The purity of the deposited sulfur was greater than 98.2%, and the structural characteristics in the XRD patterns showed that the aggregates contained quite high contents of S_8 (JCPDS Card No. 83-2284). SEM photographs show that the sulfur contents found in the glow discharge zone were in the form of irregular loose aggregates with small particle sizes, but in the quenching zone (nondischarge zone), sulfur was in the form of tight spherical aggregates with large particle sizes.

Effect of CH_4/SO_2 and applied power on sulfur selectivity

Table 1 shows the SS_S, SS_{CS_2}, and SS_{OCS} under conditions at $R = 0.3$–3.0 and applied powers $P = 30$ W and 90 W. It can be seen that the SS_S were highly dependent on R, and to some extent were affected by P. As R increased but P decreased, we found SS_S decreased. For $R \leqq 1$, no significant decrease in SS_S could be found. However, while $R = 2$ and 3, we found a significant decrease in SS_S, accompanied by an increase in both SS_{CS_2} and SS_{OCS}. Nevertheless, we found that under no circumstance was SS_{OCS} significant, but SS_{CS_2} became significant when $R = 2$ and 3 for both $P = 90$ W and 30 W. These results

Table 1. Selectivities of Sulfur-Containing Products, Including Elemental Sulfur (SS_S), CS_2 (SS_{CS_2}), and OCS (SS_{OCS}), Under Testing Conditions with Various CH_4/SO_2 Ratios and Applied Powers = 30 W and 90 W

	Selectivity					
	SS_S		SS_{CS_2}		SS_{OCS}	
CH_4/SO_2	90 W	30 W	90 W	30 W	90 W	30 W
0.3	0.989	0.969	0.001	0.013	0.010	0.019
0.5	0.980	0.950	0.003	0.024	0.017	0.027
1.0	0.940	0.847	0.038	0.101	0.022	0.052
2.0	0.523	0.357	0.447	0.502	0.030	0.141
3.0	0.449	0.293	0.481	0.543	0.070	0.164

could be explained by our proposed reaction pathways (as mentioned earlier). For $R \leqq 1$, CH_4 was the limiting reactant and the reactions were toward forming highly thermodynamically stable CO via Eq. 6, and hence resulted in the inhibition of CS generation (or CS_2 formation). When $R = 2$ and 3, we found that the decrease in SS_S was accompanied with an increase in SS_{CS_2}. This might be because part of the S content had started to react with C (provided by CH_4) to form CS_2. As for the SS_{OCS}, we found that it only increased slightly from 0.01 to 0.07 as R increased from 0.3 to 3.0. In principle, as R increased, it could be expected that CO would increase simultaneously (Eq. 6). Therefore, it also could be expected that OCS should increase accordingly (Eq. 7). However, it should be noted that OCS could be further dissociated into CO and S due to its weak bond ($D_0(OC{=}S) = 73.3$ kcal/mol). Based on this, it is not so surprising to see that OCS was a minor product in all testing conditions. Finally, this study found that the increase in P resulted in the higher SS_S but lower SS_{CS_2} and SS_{OCS}. These results clearly indicate that the higher P could be not only beneficial to the polymerization of sulfur, but also beneficial in dissociating both CS_2 and OCS. The same tendency was also found by our previous study (Tsai et al., 2002).

Effect of applied power and CH_4/SO_2 on SO_2 conversion

Figure 3a shows the conversions for both SO_2 and CH_4 (i.e., η_{SO_2} and η_{CH_4}) in the RF plasma for $R = 0$–3 conditions. For $R = 0$ (i.e., no CH_4 was introduced), we found $\eta_{SO_2} = 0.084$, which indicates that the RF plasma process was inadequate for converting pure SO_2. But as R increased (i.e., the increase of CH_4 content) to 2, we found that η_{SO_2} improved significantly to 0.968 accompanied by $\eta_{CH_4} = 0.999$. According to the proposed reaction pathways, this might be because the generated fragments CH_x and H reacted with the active species SO, O, or S, and hence reduced the probabilities of the recombination of SO_2. Figure 3a also shows that as R increased from 2 to 3, both η_{SO_2} and η_{CH_4} decreased slightly. These results might occur because the excess CH_4 molecules attached to the energetic species as R increased. Based on these findings, it is concluded that $R = 2$ would be the most appropriate ratio from the viewpoint of both high SO_2 conversion and the low CH_4 consumption rates.

Here, it should be noted that the experiments just discussed were conducted at $P = 90$ W. Therefore, this raises an important question regarding what would be the most appropriate P for converting SO_2 for this RF plasma technique. Figure 3b shows the relationships between conversions and P for experiments conducted at the $R = 2$ condition. Results show that η_{CH_4} was consistently greater than η_{SO_2} under all testing conditions. This might be because CH_4 was easily decomposed into CH_x and then formed CO and OCS (Eqs. 6 and 7), or to reform as C_2 hydrocarbons to inhibit the recombination of CH_4. While it was difficult to dissociate SO_2 into SO and O, as they would rapidly recombine into SO_2, which hence led to a lower η_{SO_2}. Nevertheless, these results clearly indicate that both η_{SO_2} and η_{CH_4} were sensitive to the applied powers. Figure 3b also shows that both η_{SO_2} and η_{CH_4} increased dramatically as P increased from 15 W to 90 W, but increased slightly as P increased from 90 W to 120 W. This might be because as P increased from 15 W to 90 W, the elevated plasma density $[e]$ was able to decompose both SO_2 and CH_4, and hence led to a significant increase in both η_{SO_2} and η_{CH_4}. Whereas, while P reached 90 W, we found that both η_{SO_2} and η_{CH_4} reached 0.968 and 0.999, respectively. This result clearly indicates that both SO_2 and CH_4 were almost decomposed at $P = 90$ W. Based on this finding, it is not too surprising to see that as P increased from 90 W to 120 W, the improvement in both η_{SO_2} and η_{CH_4} became very limited.

In conclusion, the conversion of SO_2 in the RF plasma existed at thresholds for both the CH_4/SO_2 ratio and applied power. In order to have the highest η_{SO_2} but lowest CH_4 consumption, this study suggests that the operating condition of $R = 2.0$ and $P = 90$ W would be the most appropriate combination for SO_2 conversion.

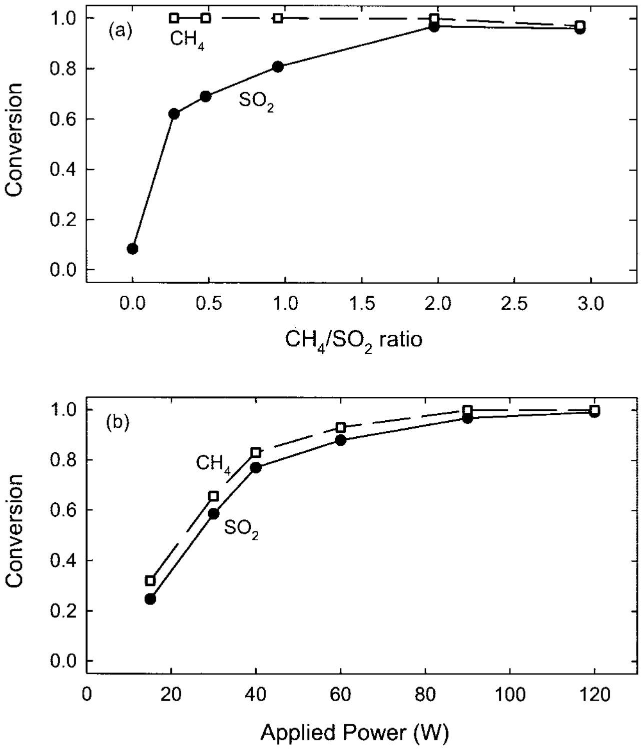

Figure 3. Conversions of SO_2 and CH_4 for (a) experiments conducted under various CH_4/SO_2 ratios at applied power = 90 W, and (b) under various applied powers at CH_4/SO_2 ratio = 2.

Acknowledgments

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