# Conversion of Carbonyl Sulfide Using a Low-Temperature Discharge Approach

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## Abstract

Carbonyl sulfide (COS) are usually yielded from the petrifaction industry or steel-making plants. In this study, a low-temperature radio-frequency (RF) plasma approach was used to destruct COS for removing sulfur. The results showed that at an inlet $O_2$/COS molar ratio of 3, the removal efficiency of COS reached 98.4% at 20 W and 4000 $N/m^2$, with the major product being $SO_2$ with small amounts of sulfur deposition. The removal efficiency of COS was lower in the $H_2$-containing condition than in the $O_2$-containing one. However, when $H_2$ was added into the COS/$N_2$ mixtures, the products, including major elemental sulfur with $CS_2$ as a minor product, were easily collected and recovered.

*Keywords:* Carbonyl sulfide; RF plasma; Destruction; Acid rain; Sulfur.

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## INTRODUCTION

Carbonyl sulfide (COS) is an odourless, tasteless and colourless polar gas molecule with a boiling point of -50.2℃, which is relatively different from other sulfur-containing impurities of hydrocarbon feedstocks (Adewuyi and Carmichael, 1987). The major emission sources of COS are the conversion of fossil fuels, steel-making plants, and waste landfills. In addition, during the high temperature stage of the Claus process, the formation of COS results from hydrocarbons being present in the flue gas according to the following reactions.

$$CO_2 + H_2S = COS + H_2O \tag{1}$$
$$CH_4 + SO_2 = COS + H_2O + H_2 \tag{2}$$
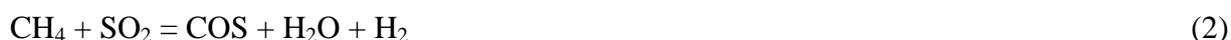
However, COS that is emitted into the atmospheric environment will not only contribute to the formation of $SO_2$ and promote photochemical reactions, but will also have an effect on the climate (Lelieveld and Heintzenberg, 1992).

The tail gas from Cluas Plants is usually incinerated and COS and $CS_2$ are converted to the harmful $SO_2$. CaO is then used as an absorbent to produce $CaSO_4$ (Borgwardt *et al.,* 1987), though it is not economically viable. An alternative method of reducing the levels of COS involves hydrogenation, which takes advantage of the hydrogen present in the Claus process via reaction (3) by using a Co-Mo-$Al_2O_3$ type catalyst (Tong *et al.,* 1992; Rhodes, *et al.,* 2000).

$$COS + 4H_2 = H_2S + CH_4 + H_2O \tag{3}$$

In addition, the removal of COS can be carried out using $SO_2$ to oxidize COS to carbon dioxide and elemental sulfur ($SO_2 + 2COS = 2CO_2 + S$) (Rhodes *et al.,* 2000). Recently, among the catalytic methods, COS hydrolysis has been recognized as the promising process due to the mild reaction conditions and higher conversion via the reaction (4) (Zhang *et al.,* 2004).

$$COS + H_2O = H_2S + CO_2 \tag{4}$$

Odorous and toxic $H_2S$ formed from reactions (3) and (4) need to be further removed using the Claus reaction ($2H_2S + SO_2 = 3S + 2H_2O$) to produce elemental sulfur (Clark *et al.,* 2001). However, some problems that are caused by the catalytic methods, such as the reduction of catalytic activity, the poison of catalysts, and product selectivities, can be further improved.

So far, the discharge process used to recover sulfur from a high concentration of COS has not been studied. A 13.56 MHz radio frequency (RF) source is commonly used in industry for generating energetic electrons (1-10 eV) to drive electron impact dissociation and penning

dissociation processes. Therefore, conventional reactions that need to be achieved at higher activation energy can now be done at a relatively low gas temperature. The RF plasma approach has been successfully applied to recover elemental sulfur from $SO_2$ and $CS_2$ (Tsai *et al.,* 2002; 2004).

Therefore, the objective of this study is to preliminarily demonstrate the RF discharge approach with a dry, low-temperature, non-catalytic, single removal process to convert COS yielding elemental sulfur and $CS_2$ that can be easily recovered. Moreover, this discharge approach did not yield the major product as $H_2S$ to avoid the requirement of the sequential Claus reaction which is converted $H_2S$ into elemental sulfur.

## EXPERIMENTAL SECTION

The experimental setup (Fig. 1) applied here is similar to that used in previous investigations on the destruction of hazardous air pollutants (Tsai *et al.,* 2004; Wang *et al.,* 2005). A laboratory scale reactor that was wrapped by two external copper electrodes coupled to a 13.56 MHz RF generator (Fritz Huttinger Elektronik Gmbh, PFG 600) with a matching network (Matchbox PFM) was used. The cylindrical glass reactor (length of 15 cm and inner diameter of 4.2 cm) was mounted vertically. An interval of about 0.6 cm-width with 1.73-slope between the two electrodes (5.5 cm-high) of copper material was set up in order to obtain an optimal matching network for the investigation. Also, to avoid their participating in the plasma-chemical reactions, the electrodes were arranged on the outside of reactor so as to create a capacitor that enables capacitive coupling power into the discharge zone.
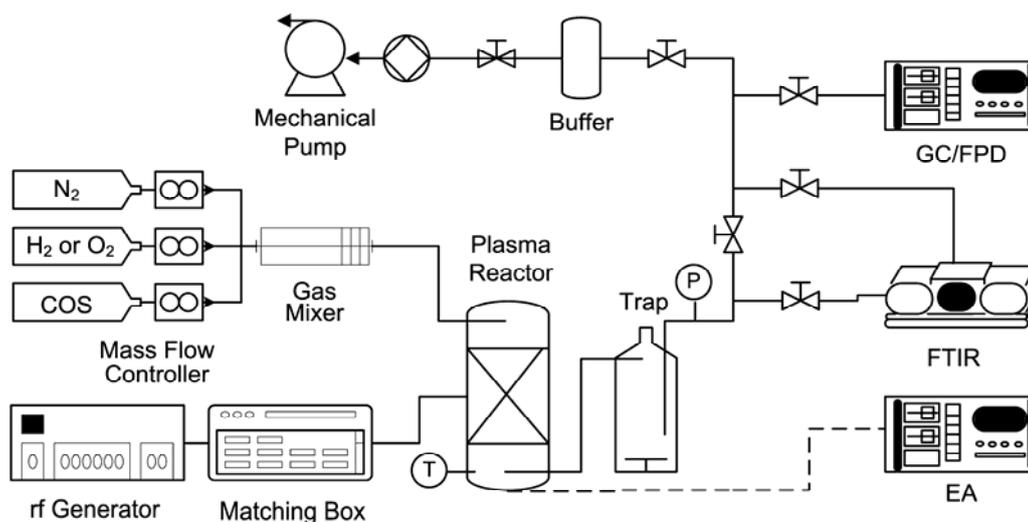


**Fig. 1.** Experimental apparatus and flowcharts.

When the reaction experiments were in process, an in-line Fourier transform infrared (FTIR) spectrometer (Bio-Rad, Model FTS-7) downstream of the reactor was used for quantifying compounds including COS, $SO_2$, $CS_2$, $CH_4$, $C_2H_2$, $C_2H_4$, CO and $CO_2$. Moreover, the samples were injected into the gas chromatograph (GC, HP 6890, column is G.S.Q, 30 m × 0.53 mm) equipped with a pulsed flame photometric detector (PFPD) to identify sulfur-containing compounds and to check the accuracy of the results.

Comprehensive ranges of experimental conditions, including an inlet $H_2$/COS molar ratio ($RH_2$) of 0-4.5, inlet $O_2$/COS molar ratio ($RO_2$) of 3, applied power (20-90 W) at room temperature (about 300 K), and an inlet COS molar fraction (COS) of 5% with a total flow rate of 200 mL/min (at STP) were probed for COS conversion. The flow rates of high-purity COS (Merck), $H_2$ or $O_2$ with balanced $N_2$, were regulated by mass flow controllers. The gases were introduced into a gas mixer, and then conducted into the RF plasma reactor to perform the experiments. All tests were done at a lower operating pressure (1333 or 4000 $N/m^2$) in order to generate and keep a discharge with a lower effluent temperature.

## RESULTS AND DISCUSSION

***Removal efficiency of COS at various inlet $H_2$/COS molar ratios and operating pressures***

In order to examine the influences of the inlet $H_2$/COS molar ratios ($RH_2$) at two levels of operating pressure on the removal efficiency of COS (RECOS), the experiments were carried out at a fixed 30 W. Fig. 2 shows that a higher RECOS can be achieved at a lower $RH_2$ and a lower pressure. As $RH_2$ increased from 0 (without $H_2$) to 4.5 at 30 W, RECOS decreased slightly from 99.8% to 97.7% at a lower pressure (1333 $N/m^2$), whereas the RECOS reduced significantly from 89.2% to 73.4% at a higher pressure (4000 $N/m^2$) (Fig. 2). At a higher operating pressure, electrons move in a shorter mean free path, resulting in lower mean electron energy that gathers a lower reaction rate of nonelastic collisions (Roth, 1995). Thus, less COS molecules were dissociated and a lower RECOS was achieved. However, because a higher pressure is preferred for practical operation in the future, the sequential experiments were carried out at 4000 $N/m^2$ to keep the discharge working. In addition, a higher $RH_2$ value means a higher feeding concentration of hydrogen, which consumes parts of the energetic species in the discharge zone and decreases RECOS.
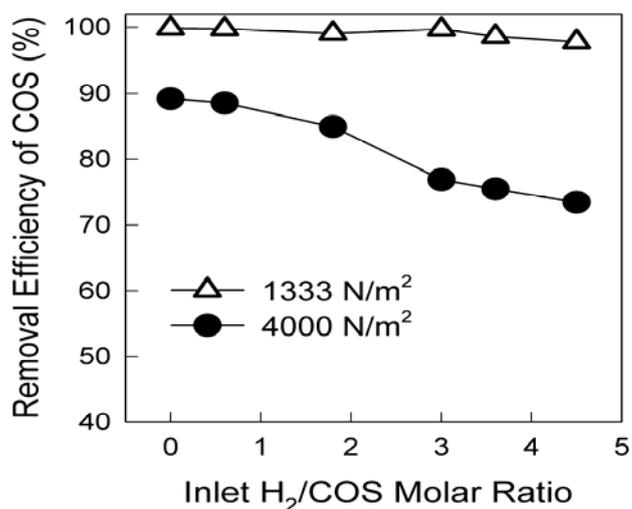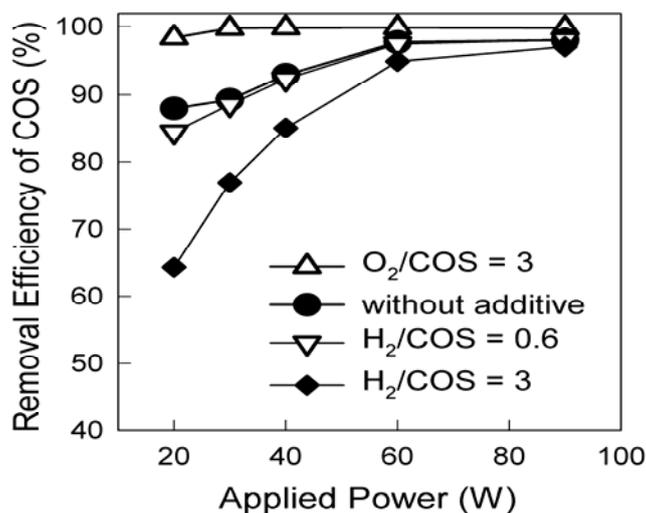
**Fig. 2.** The removal efficiencies of COS for various operating pressures and inlet $H_2$/COS molar ratios at 30 W.

### Removal efficiency of COS at various additives and applied powers

Fig. 3 shows RECOS in the RF plasma with no additive, $RO_2 = 3$, and $RH_2 = 0.6$ and 3, at an applied power of 20-90 W. For the no additive condition, RECOS increased from 88.0% to 98.0% by elevating power from 20 W to 90 W, indicating that the RF plasma process was adequate for converting pure COS in $N_2$. However, when an additive ($H_2$ or $O_2$) was added, different RECOS trends were found. The addition of $O_2$ resulted in the elevation of RECOS, while adding H2 reduced RECOS because the oxidation of COS and dissociated fragments is rapid and can prevent the recombination of COS. However, when $H_2$ molecules were added and attached to the energetic species, the reaction rate of $H_2$ or H reacting with COS or dissociated compounds was not enough to elevate RECOS, especially at a higher inlet $H_2$ concentration. When the power was increased from 20 W to 90 W, RECOS increased slightly from 98.4% to 99.8% at $RO_2 = 3$. This was much higher than the increases for $RH_2 = 3$, where RECOS rose from 64.3% to 97.0% (Fig. 3). Moreover, at $RH_2 = 0.6$, RECOS decrease only a little less than in the no $H_2$ condition.

In addition, RECOS at 20 W was apparently lower than that at 90 W except with the addition of $O_2$ (Fig. 3), which reveals that a higher discharge power results in a higher removal efficiency. This is because the larger plasma density resulted in the elevation the probabilities of electron impact dissociation or penning dissociation. However, the influence of applied power on RECOS apparently weakens at a power greater than 60 W because RECOS was greater than 95% regardless of what additive was added (Fig. 3).

**Fig. 3.** The removal efficiency of COS for various inlet $H_2$/COS molar ratios and additives at 4000 $N/m^2$

### *Comparisons of sulfur-containing products using different additives*

Though the addition of $O_2$ improved RECOS, the sulfur-containing product patterns in Table 1 revealed that the major product was harmful $SO_2$ with elemental sulfur (minor) and $CS_2$ (trace amount, the fraction of sulfur atoms that converted from COS to $CS_2$ was less than 0.2%). Because the bond dissociation energy for OS = O (131.8 kcal/mol) is much higher than that for SC = S (102.7 kcal/mol), $SO_2$ is the most dominant S-containing end product in $COS/O_2/N_2$ plasmachemical reactions and can be formed via the following reactions:

$$COS + O = SO + CO \tag{5}$$
$$O_2 + S = O + SO \tag{6}$$
$$SO + ((O+M), O_2, SO) = SO_2 + (M, O, S) \tag{7}$$

However, $SO_2$ is still an important air pollutant that causes acid deposition. Hence, adding $O_2$ to remove COS is not the best choice. A better alternative is to convert COS into mainly elemental sulfur and $CS_2$, which are easily recovered through solid and liquid form, respectively. Table 1 showed that COS with/without $H_2$ addition can be removed by yielding elemental sulfur (major, expressed as S1, which was calculated by the mass balance of S atoms) and $CS_2$ as the minor sulfur-containing product with only trace amounts of $SO_2$ (the fraction of sulfur atoms that converted from COS to $SO_2$ was about 0.2-2.96%).

**Table 1.** Comparison of sulfur-containing products after different additives were added into the COS/$N_2$ mixtures at an applied power of 20-90 W.

| Mixtures<br>Sulfur-containing products | COS without additive | Inlet $H_2$/COS ratio = 3 | Inlet $O_2$/COS ratio = 3 |
|---|---|---|---|
| Major | Elemental sulfur<br>(87.1%-94.1%)[*] | Elemental sulfur<br>(77.7%-92.8%) | SO$_2$<br>(86.6%-97.4%) |
| Minor | CS$_2$<br>(2.32%-4.98%)[*] | CS$_2$<br>(3.48%-10.8%) | Elemental sulfur<br>(2.24%-13.3%) |
| Trace | SO$_2$<br>(1.21%-2.96%)[*] | SO$_2$<br>(0.20%-0.63%) | CS$_2$<br>(0.04%-0.19%) |

[*]:in parenthesis means the mass fraction of sulfur atoms converted from COS into elemental sulfur ($S_1$), CS$_2$ or SO$_2$, respectively.

Importantly, no detectable H$_2$S was found, which is very different from traditional catalytic reactions, such as COS hydrogenation (reaction (3)) and hydrolysis of COS and CS$_2$ (reaction (4)) that produce H$_2$S as the major product first, and then remove H$_2$S via producing elemental sulfur through the Claus reaction. The results indicate that the RF discharge process can directly convert COS into recoverable elemental sulfur or CS$_2$ with/without H$_2$ addition. Moreover, no H$_2$S is yielded because the bond dissociation energy of HS-H (92.0 kcal/mol) and S-H (83.5 kcal/mol) in H$_2$S was apparently lower than that of SC = S (102.7 kcal/mol) and C = S (170.5 kcal/mol) in CS$_2$. Hence, CS$_2$ is more thermodynamic stable than H$_2$S. In addition, even H$_2$S was yielded; it would be easily dissociated through reacting with O to form SO as the precursor of product SO$_2$. These properties favored the existence of CS to the formation of CS$_2$ other than H$_2$S in the H$_2$/COS/N$_2$ plasma.

However, the difference between H$_2$ and no H$_2$ addition conditions is the yield of sulfur-containing products: more elemental sulfur and SO$_2$ were found in the no H$_2$ environment (that is, COS plasmalysis), while more CS$_2$ was detected when H$_2$ was added. CS$_2$ can be easily recovery in liquid form when the temperature is lower than the boiling point (46.25℃); hence, CS$_2$ can be more easily collected than elemental sulfur, making the H$_2$/COS/N$_2$ plasma approach a potential solution.

## CONCLUSIONS

In this study, high concentration of COS was successfully destructed and converted into other sulfur-containing products by adding $H_2$ or $O_2$, or without an additive, utilizing a low-pressure RF discharge approach. The important finding is that no $H_2S$ was detected, which is very different from the traditional catalytic removal process, including COS hydrogenation ($COS + 4H_2 = H_2S + CH_4 + H_2O$) and hydrolysis of COS and $CS_2$ ($COS + H_2O \rightarrow H_2S + CO_2$). The discharge approach replaced major product $H_2S$ with elemental sulfur that can be easily recovered with or without $H_2$, 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.

## ACKNOWLEDGMENTS

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